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SUPERINDUSTRIA Y COMERCIO
Radicacion : 00044-92 00000003 Folios: 2
Fecha (AMD): 2002-0-09 11:56:35
Tramite : 002 PATENTES D 1 REGISTRO/ 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

SEÑORES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
MINISTERIO DE DESARROLLO ECONOMICO

REF SOLICITUD No 00048492
SOLICITANTE BP EXPLORATION OPERATING COMPANY LIMITED
SOLICITUD No 00048492
FECHA SOLICITUD JUNIO 28, 2000
PATENTE MICROEMULSIONES DE UTILIDAD EN UN METODO
PARA INTRODUCIR UN PRODUCTO QUIMICO EN
UNA FORMACION DE ROCA QUE COMPRENDE
PETROLEO Y/O GAS PARA LA EXPLOTACION DE UN
YACIMIENTO DE PETROLEO O GAS

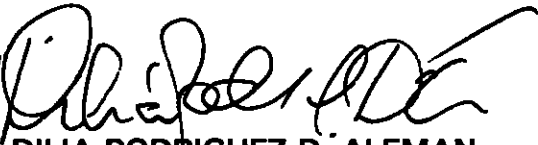
SOLICITUD DE ESTUDIO DE FONDO

DILIA RODRÍGUEZ D'ALEMAN, en mi condición de apoderada de la Sociedad solicitante, por el presente escrito atentamente solicito a Usted que habiéndose surtido la publicación de la presente solicitud, en la Gaceta de la Propiedad Industrial N°.516 de fecha Mayo 30 de 2002 se proceda con el estudio de Fondo

Para tal fin me permito anexar la tasa correspondiente Recibo No 02 61 868

Agradezco continuar con el presente trámite

Señor Jefe,



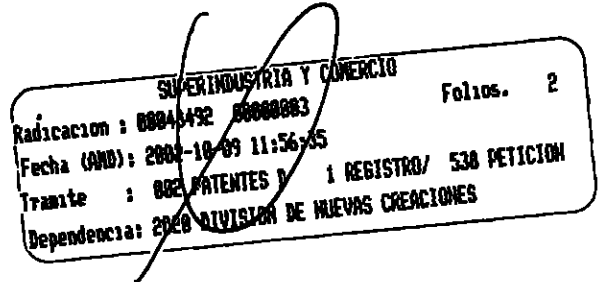
DILIA RODRIGUEZ D'ALEMAN
C C 41 654 882 de Bogotá
T P 20824 del C S J

P-347

66 62

Industria y Comercio
SUPERINTENDENCIA

NIT . 800176089-2



RECIBO OFICIAL DE CAJA : 02 - 61,868
FECHA : SEPTIEMBRE 16 DE 2002

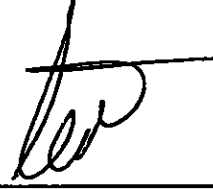
***** C O N S I G N A C I O N *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No	PAGO	FECHA PAGO	Vr. PAGO
CLARKE MODET Y CA	COLONB	CONSIGNACION	BANCO POPULAR	050-00110-6	4801691	16/09/2002	2,089,800 00

***** C O N C E P T O *****

CANT	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN
		TOTAL :	\$ 318,000.00

SON: TRESCIENTOS DIEZ Y OCHO MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No _____

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020
Bogotá, D C , 11 de Mayo de 2005

Doctora
DILIA RODRÍGUEZ D'ALEMAN
Representante **BP EXPLORATION OPERATING COMPANY LIMITED**

ASUNTO	Radicación No	00-48492
	Trámite	002
	Evento	001
	Actuacion	430
	Oficio	12801
	Folios	143

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica

1) Documentos estudiados:

- Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 50 a 62 de la solicitud en estudio
- Para el presente estudio se tendrá en cuenta el capítulo reivindicatono que comprende 17 reivindicaciones en los folios 63 a 64 de la solicitud en estudio
- Conforme lo establece los artículos 9, 10 y 11 de la decision 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 28 de junio de 2000, y en el momento de la radicación SI se reclamo priondad de la primera solicitud presentada en Gran Bretaña GB9915214 2

2) Objeto de la invención

- Las reivindicaciones 1 a 17 de la solicitud en estudio se refieren a una micro emulsion que comprende (i) una fase oleosa, (ii) una fase acuosa que comprende una solución acuosa de un producto químico soluble en agua para la explotación de un yacimiento de petróleo o de gas o una dispersión acuosa de un producto químico dispersable en agua para la explotación de un yacimiento de petróleo o de gas y (iii) al menos un surfactante, caracterizada porque la fase acuosa esta distnbuida en la fase oleosa en forma de gotitas que tienen un diámetro del orden de 1 a 1 000 nm o en forma de micro dominios que tienen al menos una dimensión de longitud, ancho y espesor del orden de 1 a 1000 nm
- El anterior producto busca mejorar la explotación de yacimientos de hidrocarburos

- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 09 K 7/002

3) Claridad de la Solicitud

- a) El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones establece

"La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

Aunque no se establece claramente y con detalle en la legislación la forma de presentar una solicitud, universalmente se siguen unos parámetros para facilitar su estudio. La forma de presentación de la presente solicitud, no permite una lectura fácil dado el tamaño de la letra. Se recomienda al solicitante enviar un nuevo texto completo con un tamaño de letra adecuado.

- b) El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

"Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará reivindicación dependiente múltiple."

El capítulo reivindicativo no es claro toda vez que

- i) No se encuentra correctamente redactado. Dadas las muchas explicaciones que da el solicitante en las reivindicaciones, se torna confuso el identificar el objeto a ser protegido. Por su estructura todas las reivindicaciones deben constar de dos partes. Una primera parte, el preámbulo, sirve para situar el objeto de la invención dentro de un contexto técnico, es lo que se conoce y sobre lo que no se reclama ningún privilegio. Si el solicitante en esta parte afirma que quiere proteger una micro emulsión, no es necesario que explique que comprende una fase acuosa, una fase oleosa y por lo menos un surfactante, pues todas las micro emulsiones tienen esas características y un técnico medio lo sabe. Además, si se habla de un producto químico dispersable en agua, se puede afirmar que dicho producto es soluble en agua. Por lo tanto ese preámbulo largo tedioso y confuso, puede quedar reducido a "Micro emulsión que incorpora un producto químico soluble en agua para mejorar la explotación de un

yacimiento de petróleo o de gas, caracterizado por " Se entendería por el escrito, que la segunda parte (o parte característica, que define lo que se considera novedoso y se desea proteger), consiste en la distribución de la fase acuosa en la fase oleosa Debe corregirse el capítulo

- ii) La reivindicación 12 no aporta ningún elemento técnico nuevo y solo se evidencia un uso que se le quiere dar al compuesto de las primeras reivindicaciones Por tanto, dicha reivindicación no puede ser aceptada y debe eliminarse
- iii) La reivindicación 17 no revela ninguna característica técnica válida que permita identificar o caracterizar un producto Se trata sólo de una apreciación subjetiva (aumentar eficacia) Debe eliminarse esta reivindicación
- iv) Las reivindicaciones no encuentran soporte en la descripción Como se observa en la reivindicación 1, el solicitante quiere que se le proteja una micro emulsión con ciertas características, que son las mismas que en el folio 52 dice el mismo solicitante son conocidas Existe una clara contradicción

De acuerdo a lo anterior, el capítulo reivindicatono no cumple con el requisito de claridad de acuerdo a lo establecido en el Art 30 de la Decisión 486

4) Reivindicaciones de uso

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece

"Los Países Miembros otorgarán patentes para las invenciones sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial"

Las reivindicaciones 13 y siguientes simplemente corresponden a un uso del producto, mas no están caracterizando un método nuevo El producto químico que sirve para los pozos necesariamente se debe inyectar dentro del pozo, en ocasiones se inunda y siempre se deja que actúe el producto en la formación Es evidente que lo único que se pretende acá es proteger el uso del producto

Tal como se dijo en líneas anteriores, es evidente que la reivindicación 12, además de su mala redacción, evidencia la protección de un uso

Tal como esta contemplado en la legislación el uso no se protege Se protegen los productos o procedimientos, donde el producto este correctamente definido por su conformación o su composición, y los procedimientos por la serie de etapas que busquen un fin El uso no corresponde ni a un uso ni a un procedimiento El uso es simplemente la aplicación industrial de esos productos o procedimientos

Por lo anterior, las reivindicaciones 12 a 16 no son patentables de acuerdo al Art 14 de la Decisión 486

5) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece

"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida "

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40 "

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 09 K 7/02 y las más cercanas a ellas, se encontró que antes del 29 de junio de 1999 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con micro emulsiones

De acuerdo con o establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente

Nº	Documento	Título	Fecha de Publicación
D1	US 5186257	Polymers useful in the recovery and processing of natural resources	16 02 1993
D2	US 4741399	Oil recovery process utilizing gravitational forces	03 05 1988
D3	US 4681912	Process for manufacturing inverse microlatices of water soluble copolymers, the resultant inverse microlatices and their use for improving the production of hydrocarbons	21 07 1987
D4	US 4012329	Water in oil micro emulsion drilling fluids	15 03 1977
D5	US 3688851	Treating subsurface formations	05 09 1972
D6	US 3670816	Oil recovery process	20 06 1972
D7	US 3254714	Use of micro emulsions in miscible type oil recovery procedure	07 06 1966

6) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial"

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio

a) Evaluación de la novedad y el del Nivel Inventivo

El art 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece

"Una invención se considerará nueva cuando no está comprendida en el estado de la técnica " "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida "

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fechas de prioridad cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40 "

El art 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece

"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica"

El documento D1 US 5186257 muestra una sene de polímeros empleados en yacimientos, los cuales son aplicados en forma de micro emulsión Todo lo que muestra la presente solicitud se puede derivar de D1

De la misma forma **D2 US 4741399** revela métodos donde la inyección de compuestos (algunos enumerados en la presente solicitud) mejora el rendimiento de pozos de hidrocarburos Combinando este documento con uno cualquiera de los demás documentos citados se permite llegar a lo que el solicitante desea proteger para Colombia

D3 US 4681912 muestra micro emulsiones de copolímeros solubles en agua dentro de una fase oleosa junto con surfactante(s) que mejoran las características de los pozos de hidrocarburos Partiendo de D3, un técnico medio puede llegar a lo que se quiere proteger en la presente solicitud

Igualmente **D4 US 4012329** muestra micro emulsiones como las esbozadas en la presente solicitud y que también se usan en perforaciones de hidrocarburos Se evidenciaría la presente solicitud partiendo de D4 Muchas de las ventajas que teóricamente obtiene el solicitante ya habían sido descubiertas por la antenondad

D5 US 3688851 o D6 US 3670816 mencionan emulsiones que cumplen con el mismo objetivo propuesto en la presente solicitud Al combinar uno de estos documentos con otro cualquiera de los enumerados se encuentra lo que el solicitante desea proteger para Colombia

D7 US 3254714 también revela el uso de micro emulsiones para el tratamiento de pozos

b) Resumen

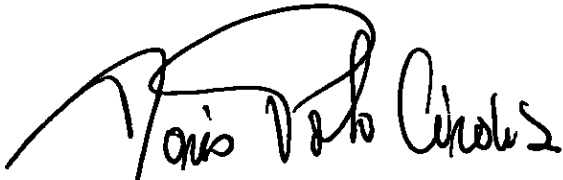
En conclusion los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así

Nº	Documento	Rervindicaciones afectadas	Requisito que afecta
D1	US 5186257	1 - 17	Novedad
			Nivel inventivo
D2	US 4741399	1 - 17	Nivel inventivo
D3	US 4681912	1 – 17	Novedad
			Nivel inventivo
D4	US 4012329	1 – 17	Novedad
			Nivel inventivo
D5	US 3688851	1 – 17	Nivel inventivo
D6	US 3670816	1 – 17	Nivel inventivo
D7	US 3254714	1 - 17	Novedad
			Nivel inventivo

7) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente

Notifíquese el presente oficio conforme a lo dispuesto por el numeral 5 2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001


DORIS POLO CORDOBA
Jefe División de Nuevas Creaciones (E)

El anterior requerimiento fue notificado por fijación en la lista, de fecha

19 MAYO 2005

Concepto Técnico N°	EXAMINADOR TÉCNICO	EXAMINADOR JURÍDICO
663	Código No 202003	Código No

97
74



United States Patent [19]
Stahl et al.

US005186257A
[11] Patent Number: 5,186,257
[45] Date of Patent: Feb. 16, 1993

- [34] POLYMERS USEFUL IN THE RECOVERY AND PROCESSING OF NATURAL RESOURCES
- [75] Inventors Allan Stahl, Humble, Tex., Ahmad Moradi-Araghi, Bartlesville, Okla., John Westerman, Wadsworth, Ohio; Henry L. Hsieh, Bartlesville, Okla., James H. Hedges, Bartlesville, Okla., Gehr Bjornson, Bartlesville, Okla.
- [73] Assignee Phillips Petroleum Company, Bartlesville, Okla
- [21] Appl No 805,283
- [22] Filed Dec 10, 1991

Related U.S. Application Data

- [60] Division of Ser No. 568,363, Jan 9, 1984, Pat No 4 951,921 which is a continuation-in-part of Ser No 461,707, Jan 28, 1983 Pat No. 4 644,020.
- [51] Int. Cl.³ E21B 43/22
- [52] U.S. Cl. 166/273, 166/274
- [58] Field of Search 166/273, 274, 252/8 554

References Cited

- [36] U S PATENT DOCUMENTS
- 2,810,716 10/1957 Markus
- 2,827,964 3/1958 Sandiford et al
- 2,923,734 2/1960 Sheetz
- 2,938,017 5/1960 Grosser
- 2,961,431 11/1960 Kutner
- 2,964,357 12/1960 Niederhauser et al
- 3,006,900 10/1961 Fikentscher et al.
- 3,025,234 3/1962 Cantenno
- 3,039,529 6/1962 McKenna
- 3,094,504 6/1963 Murdock et al.
- 3,129,210 4/1964 Grosser et al
- 3,146,193 8/1964 Sullivan
- 3,179,171 4/1965 Beale, Jr

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

- 0094898 11/1983 European Pat. Off.
- 0095730 12/1983 European Pat. Off
- 1591552 6/1981 United Kingdom

OTHER PUBLICATIONS

- Bleakley, "BP Faces North Sea Challenges", *Petroleum Engineer International*, pp 29-32, 34-35, and 38, Oct 1982.
- Chatterjee, "Solvent Effects in Free Radical Copolymerization", *Canadian Journal of Chemistry*, vol 49, pp. 3249-3251 (1971).

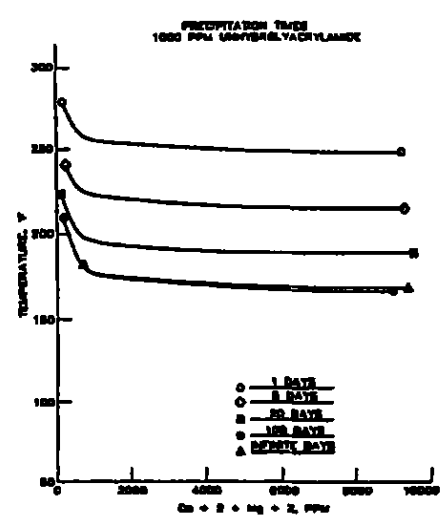
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Primary Examiner—George A. Suchfield
Attorney, Agent, or Firm—Gary L. Haag

[57] ABSTRACT

Water-soluble polymers comprising N-vinyl amide such as an N-vinyl lactam are found to be useful in processes wherein the polymer is introduced into a subterranean wellbore. Polymers useful in the recovery of natural resources are prepared by polymerizing an N-vinyl lactam by free radical initiation with polymerization conducted in an aqueous solution polymerization medium preferably containing a mixture of dissolved electrolytes, or in a polymerization medium consisting essentially of a tertiary alkanol. Copolymers of such N-vinyl lactams with unsaturated amides and terpolymers prepared by polymerizing an N-vinyl lactam and an unsaturated amide with a selected monomer compound are also useful when prepared by these methods. The invention also broadly encompasses utilizing a water-soluble polymer comprising at least one of a hydrophobic vinyl-containing sulfonate, phosphonate or ester and/or hydrophilic N-vinyl lactam for applications under hostile conditions.

13 Claims, 16 Drawing Sheets



U S PATENT DOCUMENTS

3,203,938	8/1965	Beechtold	3,806,367	4/1974	Lange et al
3,215,680	11/1965	Kolodny	3,816,308	6/1974	Le Blanc
3,219,498	11/1965	Nitzsche et al	3,820,603	6/1974	Knight et al
3,223,162	12/1965	Burge	3,841,402	10/1974	Knight et al
3,256,141	6/1966	Stephenson	3,849,165	11/1974	Stahly et al
3,336,269	8/1967	Monagle et al	3,858,652	1/1975	Rhody et al
3,336,270	8/1967	Monagle	3,862,915	1/1975	Fried et al
3,397,232	8/1968	Takagi et al	3,877,522	4/1975	Knight et al
3,397,744	8/1968	Hort et al	3,898,037	8/1975	Lange et al
3,403,106	10/1968	Scanley	3,907,927	9/1975	Guilbault
3,421,584	1/1969	Eilers et al	3,908,760	9/1975	Clampitt et al
3,423,367	1/1969	Merjan et al	3,909,423	9/1975	Hessert et al
3,434,971	3/1969	Atkins			
3,450,680	6/1969	Jursich et al			
3,459,720	8/1969	Grosser et al			
3,468,832	9/1969	Barabas et al			
3,490,533	1/1970	McLaughlin			
3,500,925	3/1970	Beiswanger			
3,506,707	4/1970	Miller et al			
3,511,313	5/1970	Eilers et al			
3,541,059	11/1970	Schaper			
3,547,899	12/1970	Art et al			
3,558,545	1/1971	Lummas			
3,629,101	12/1971	Hille et al			
3,630,868	12/1971	Marans			
3,679,000	7/1972	Kaufman			
3,679,900	7/1972	Kunura			
3,681,215	8/1972	Peterson			
3,686,150	8/1972	Barabas et al			
3,689,439	9/1972	Field et al			
3,727,687	4/1973	Clampitt et al			
3,728,319	4/1973	Kiesel et al			
3,749,172	7/1973	Hessert et al			
3,776,310	12/1973	Norton et al			
3,793,276	3/1974	Eilers et al			

(List continued on next page)

OTHER PUBLICATIONS

Chatterji, "Applications of Water-Soluble Polymers in the Oil Field", *Journal of Petroleum Technology*, Nov 1981, pp 2042-2056

Davison and Mentzer, SPE 9300, "Polymer Flooding in North Sea Oil Reservations" presented at 55th Annual Fall Technical Conf of Society of Petroleum Engineers, AIME, Dallas, Texas, Sep 21-24, 1980 (semicon) later published in *Society of Petroleum Engineers Journal*, Jun. 1982, pp. 353-362.

Foshee et al, SPE 6202, "Preparation and Testing of Partially Hydrolyzed Polyacrylamide Solutions" presented at 51st Annual Fall Technical Conference of Society of Petroleum Engineers of AIME, New Orleans, Oct. 3-6, 1976.

Klemmensen and Bauer, "Water Soluble Acrylic Polymer for Enhanced Oil Recovery," *Polymer Preprints* vol. 22, Aug 1981, pp 78-80.

(List continued on next page)

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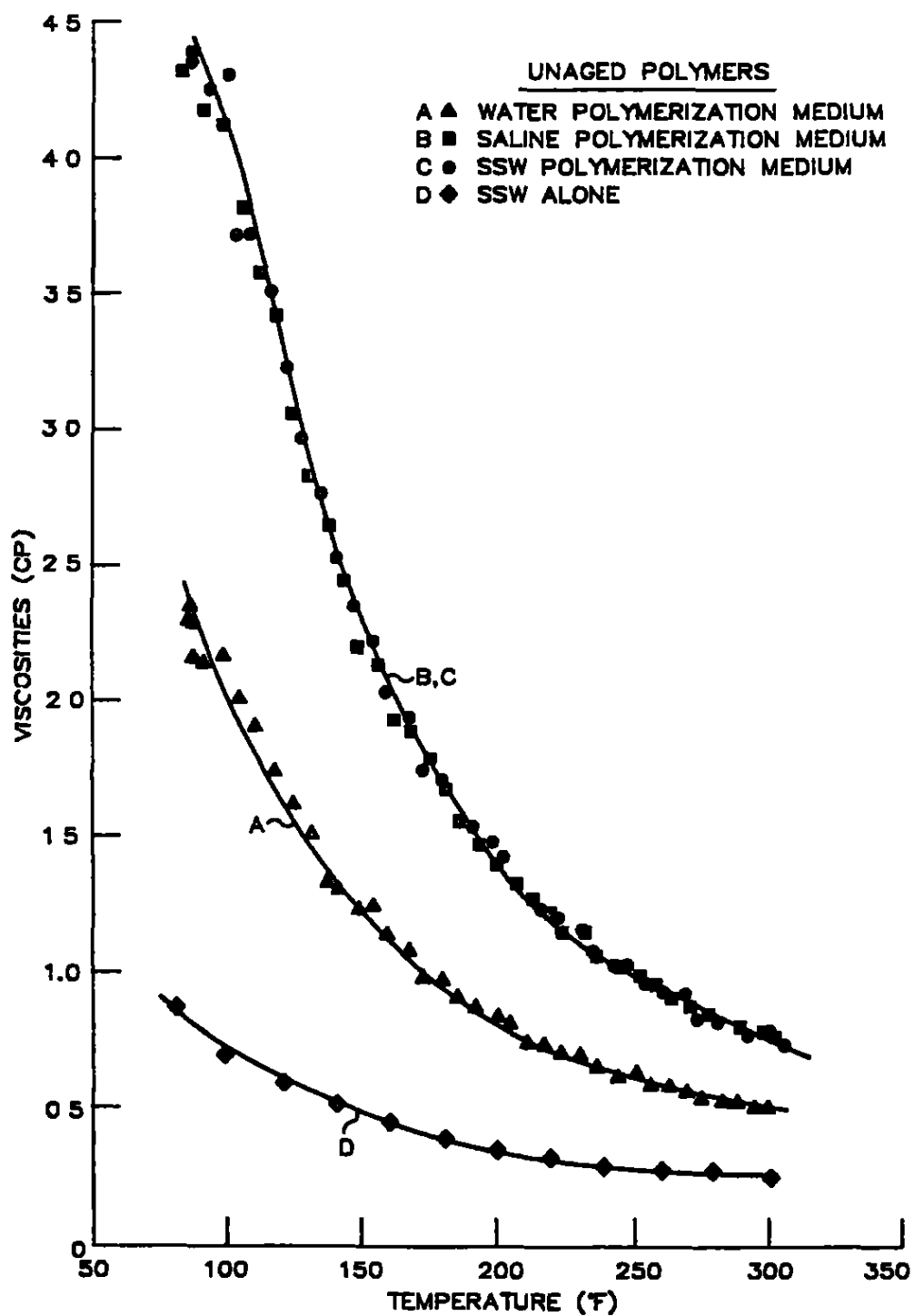
U. S. PATENT DOCUMENTS

3,929,741 12/1975 Laakey
3,931,089 1/1976 Kari
3,933,303 1/1976 Khromov
3,937,633 2/1976 Knight et al
3,948,740 4/1976 Phalangas
3,948,783 4/1976 Szaba et al
3,953,341 4/1976 Martin
3,993,133 11/1976 Clampitt
4,016,932 4/1977 Kalfagiou
4,024,040 5/1977 Phalangas et al
4,040,967 8/1977 Nimerick et al
4,048,077 9/1977 Engelhardt et al
4,048,377 9/1977 Boschetti et al
4,057,533 11/1977 Hort et al
4,066,324 1/1978 Phalangas
4,098,337 7/1978 Argabright et al
4,122,895 10/1978 Sifton et al. 166/273 X
4,125,156 11/1978 Ohmmann - - - - - 166/273 X
4,137,969 2/1979 Phalangas et al
4,190,109 2/1980 Barton, Jr
4,207,946 6/1980 Haltmar et al.
4,210,205 7/1980 Allen et al
4,219,429 8/1980 Allen et al
4,236,545 12/1980 Knight et al
4,246,124 1/1981 Swanson
4,248,304 2/1981 Phillips
4,254,249 3/1981 Cottrell et al.
4,260,713 4/1981 Tanaka et al.
4,265,308 5/1981 Hedges et al. 166/273 X
4,277,580 7/1981 Allen et al
4,294,949 10/1981 Karrer

4,300,634 11/1981 Clampitt
4,304,300 12/1981 Watson
4,309,523 1/1982 Engelhardt et al
4,323,463 4/1982 Morduchowitz
4,326,970 4/1982 Cottrell et al
4,337,215 6/1982 Doi et al.
4,353,806 10/1982 Canter et al
4,404,111 9/1983 Bi et al
4,423,123 12/1983 Okamoto
4,440,228 4/1984 Swanson
4,451,351 5/1984 Porter et al
4,461,351 7/1984 Falk
4,471,097 9/1984 Klaus et al. 526/240

OTHER PUBLICATIONS

Park, Scott and Lummus, "Obtaining Low Solids Drilling Fluids", *Oil and Gas Journal*, vol 58, pp 81-84, May 30, 1960.
Dept. of Energy report, DOE/BETC/5603-10, published Jun 1980, pp. 5/6, 117/118 and 137
Jennings, Rogers and West, "Factors Influencing Mobility Control by Polymer Solutions," *Journal of Petroleum Technology*, Mar 1971, pp 391-401
Encyclopedia of Polymer Science and Technology, vol 14, "Vacuumetry", pp 717-722, 1971
Kirk-Othmer, *Encyclopedia of Chemical Technology*, Third Edition, vol 18, pp 734-736 (1982).
Kirk-Othmer, *Encyclopedia of Chemical Technology*, Third Edition vol 18 "Polyelectrolysis," pp. 495-530 (1982)

**FIG. 1**

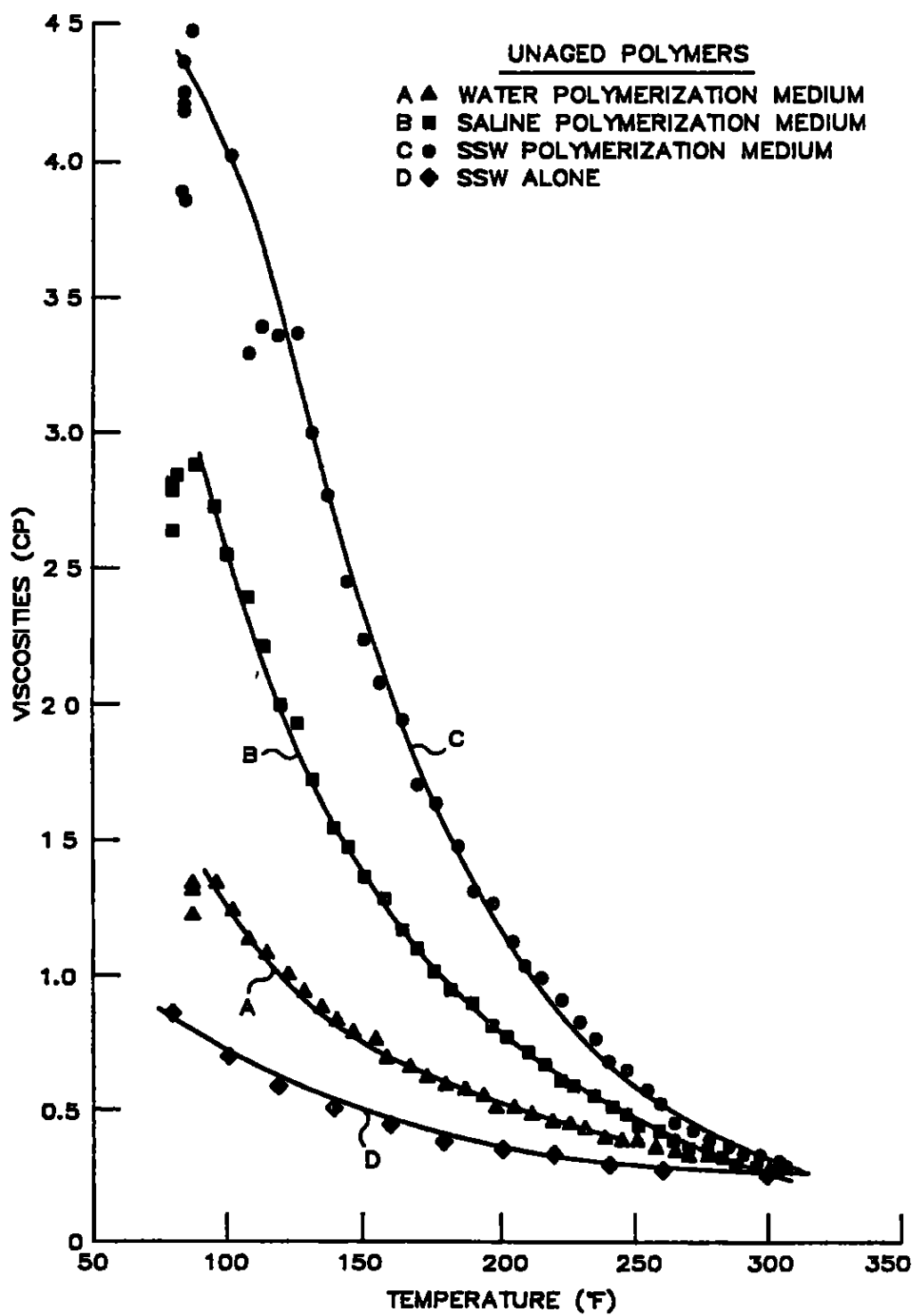


FIG. 2

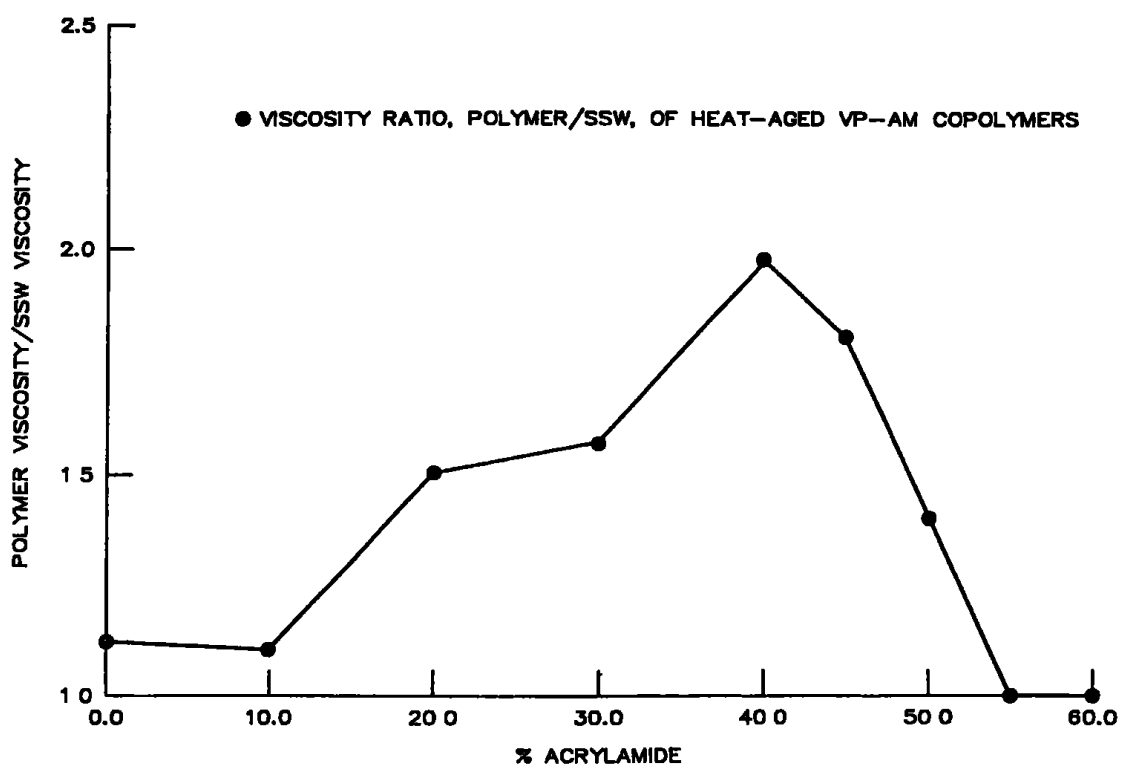


FIG. 3

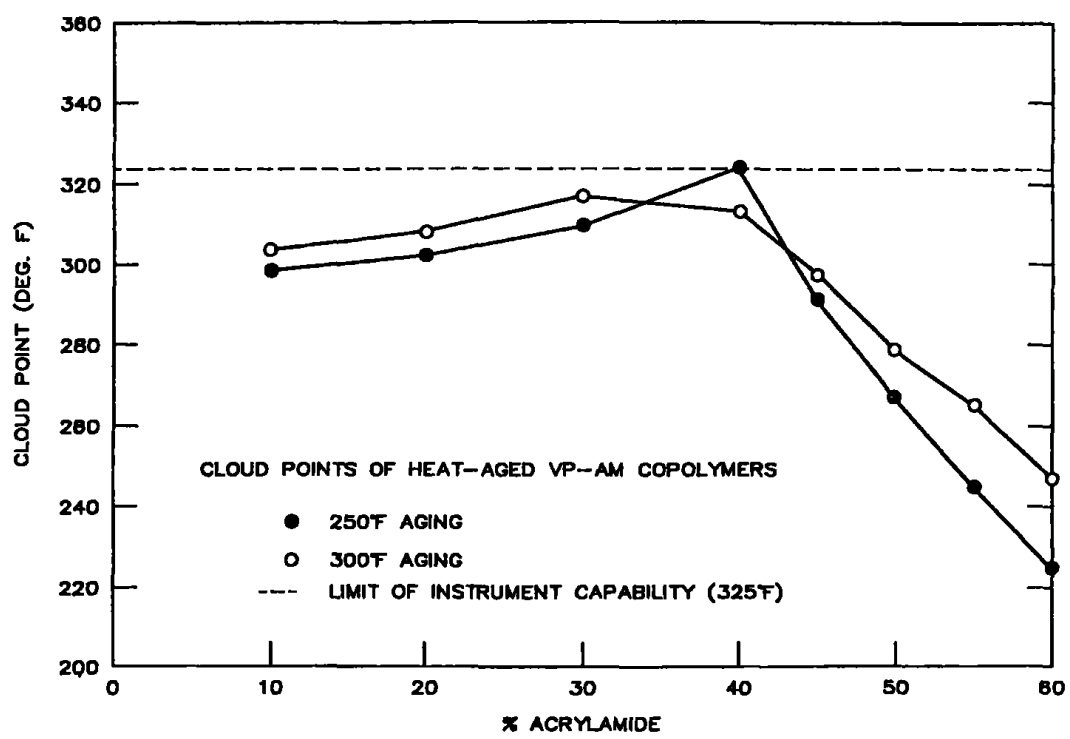


FIG. 4

80

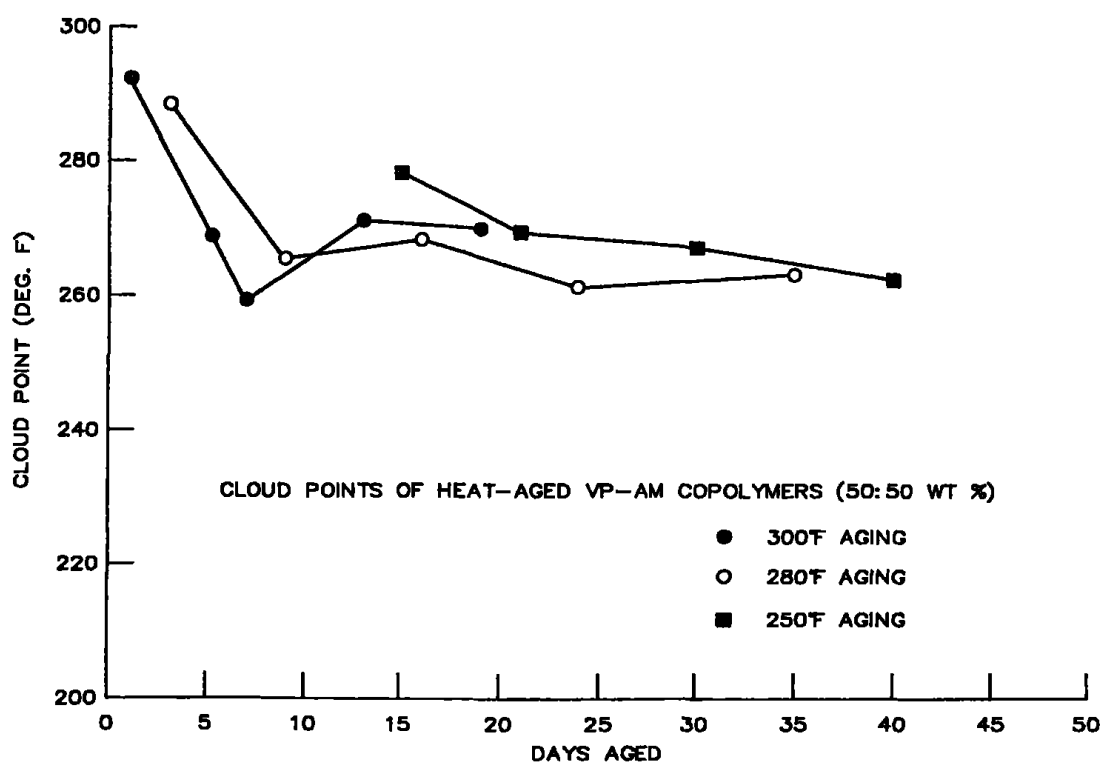


FIG. 5

91

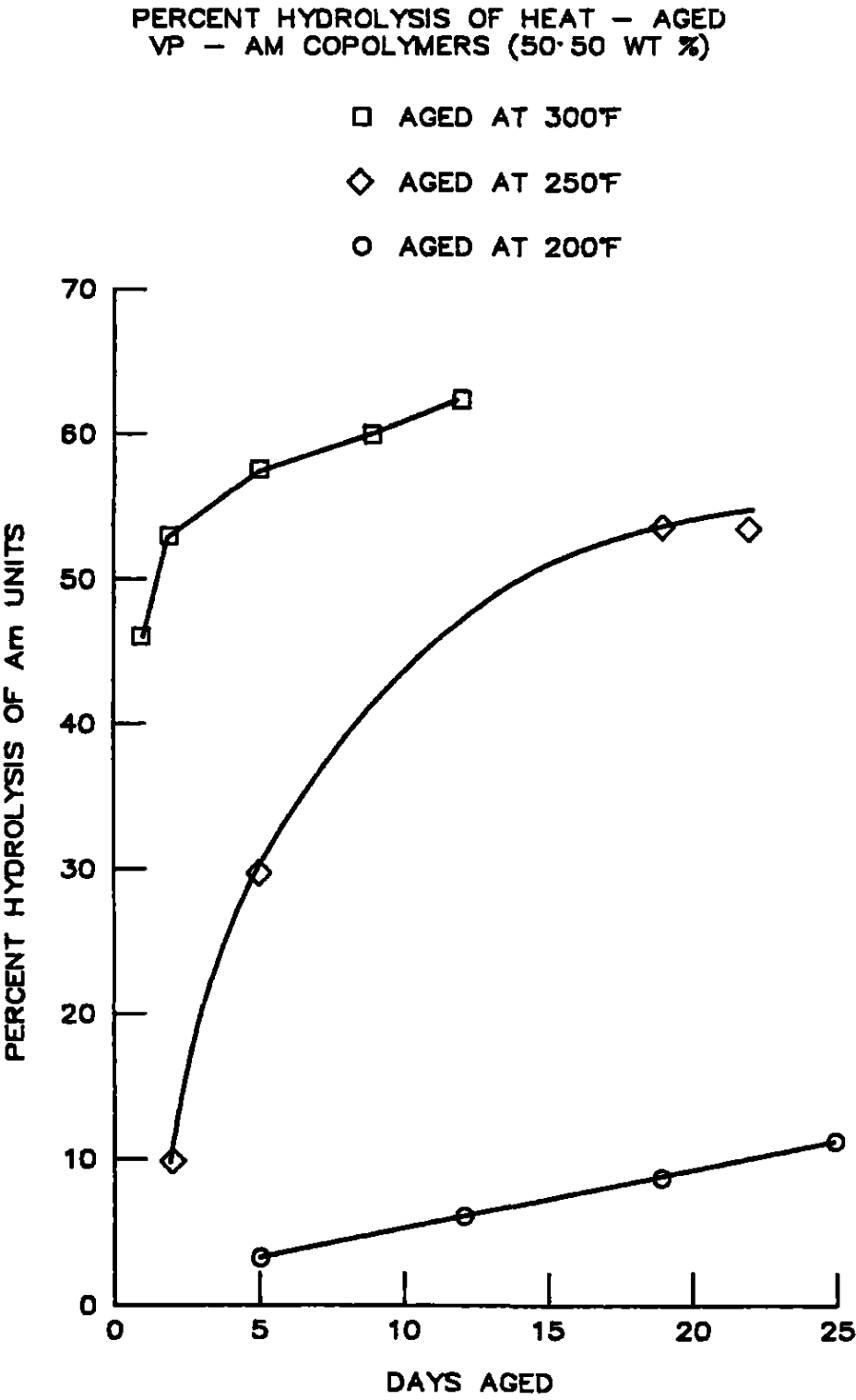


FIG. 6

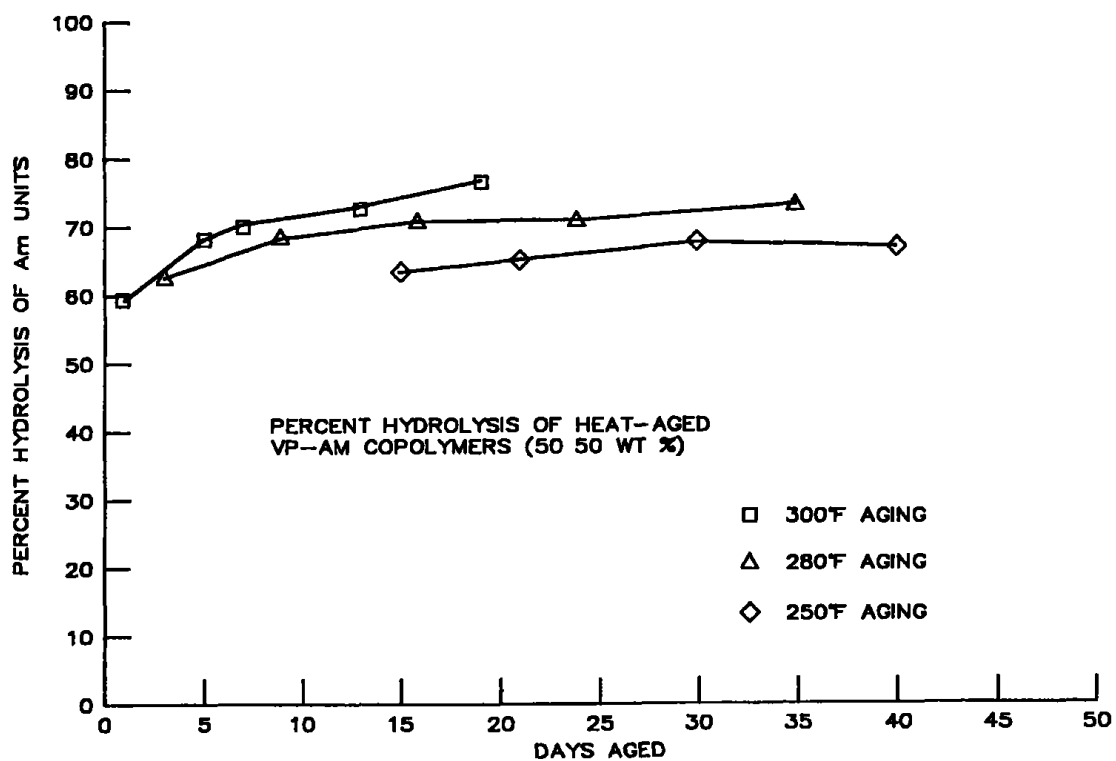
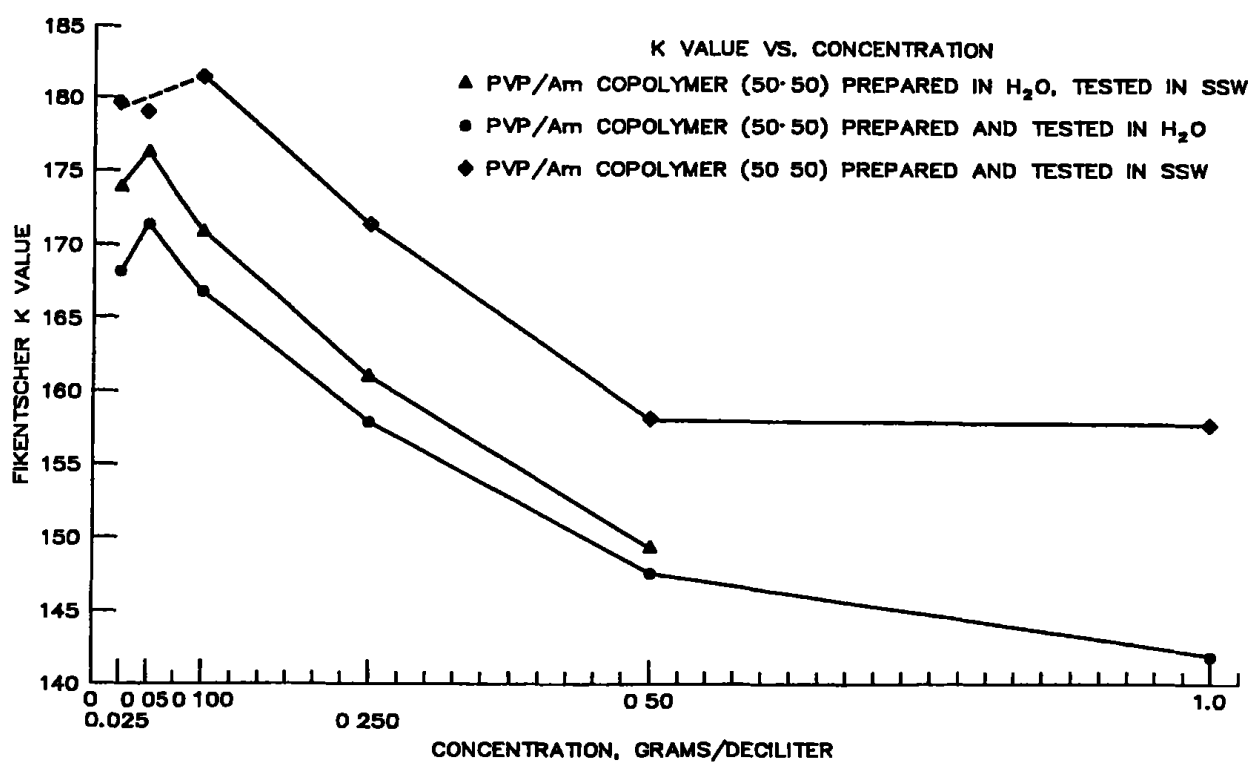
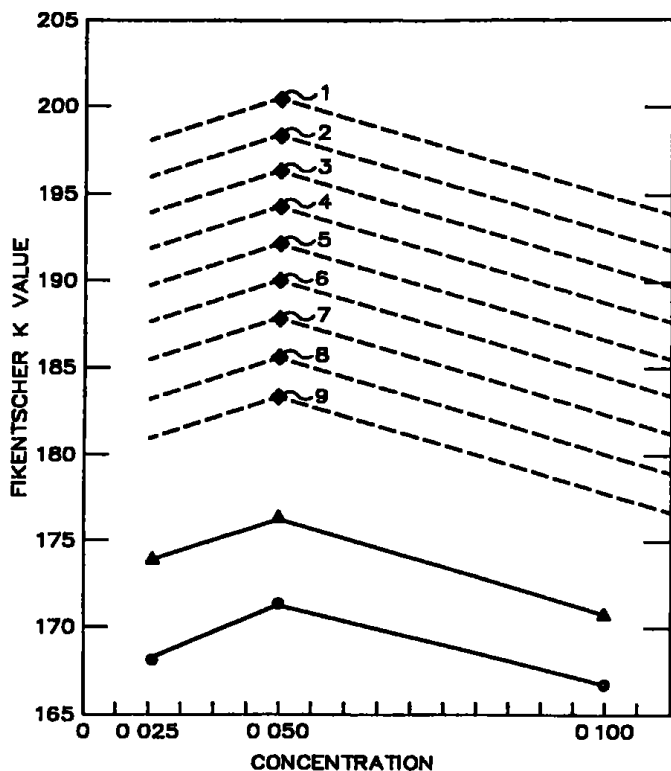


FIG. 7

83
86





K VALUE VS CONCENTRATION

- ▲ PVP/Am COPOLYMER (50 50) PREPARED IN H₂O, TESTED IN SSW
- PVP/Am COPOLYMER (50 50) PREPARED AND TESTED IN H₂O
- ◆ PVP/Am COPOLYMER (50 50) PREPARED AND TESTED IN SSW AS INDICATED:

POINT	POLY MED.	TEST MED.
(1)	SSW	SSW
(2)	SSW	NaCl, CaCl ₂ , MgCl ₂
(3)	SSW	H ₂ O
(4)	SSW(II)	SSW
(5)	NaCl	SSW, NaCl
(6)	NaCl+MgCl ₂	H ₂ O
(7)	NaCl	MgCl ₂ , CaCl ₂ , SSW, H ₂ O
(8)	CaCl ₂	MgCl ₂
(9)	MgCl ₂	SSW, CaCl ₂ , NaCl
(10)	NaCl+MgCl ₂	H ₂ O, CaCl ₂ , MgCl ₂ , NaCl, SSW
(11)	NaCl+MgCl ₂	NaCl, SSW
(12)	NaCl+MgCl ₂	CaCl ₂
(13)	NaCl+MgCl ₂	MgCl ₂

FIG. 9

88

89
86

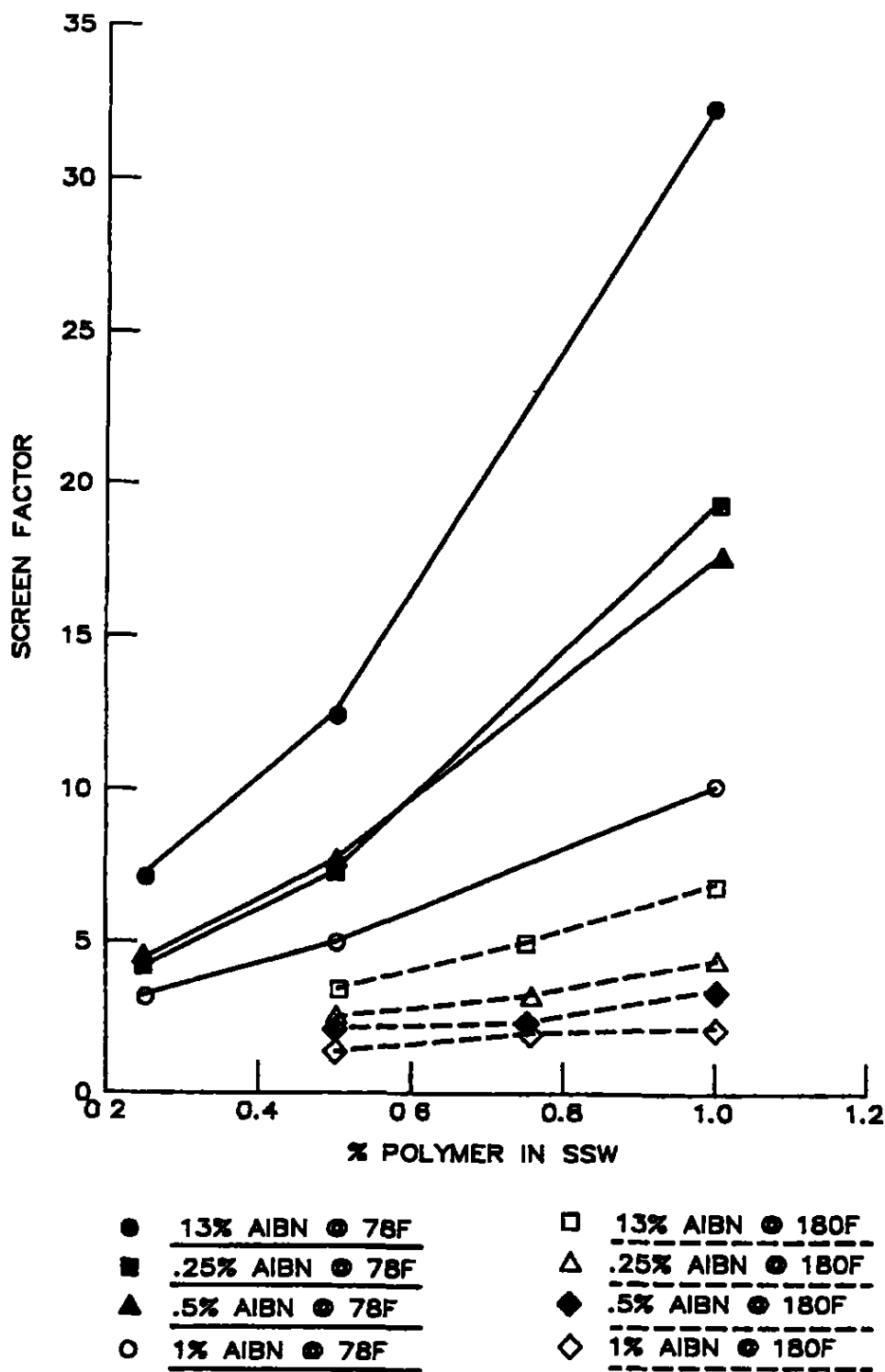


FIG. 10

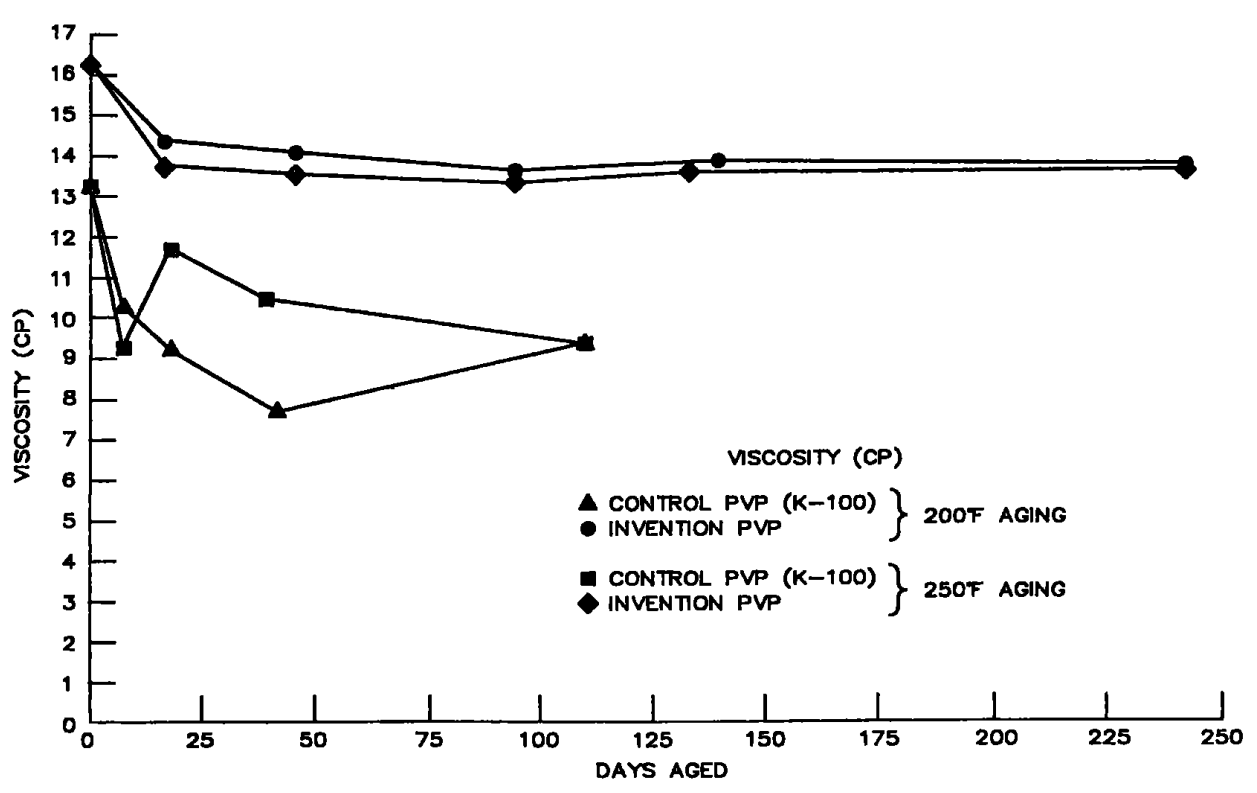
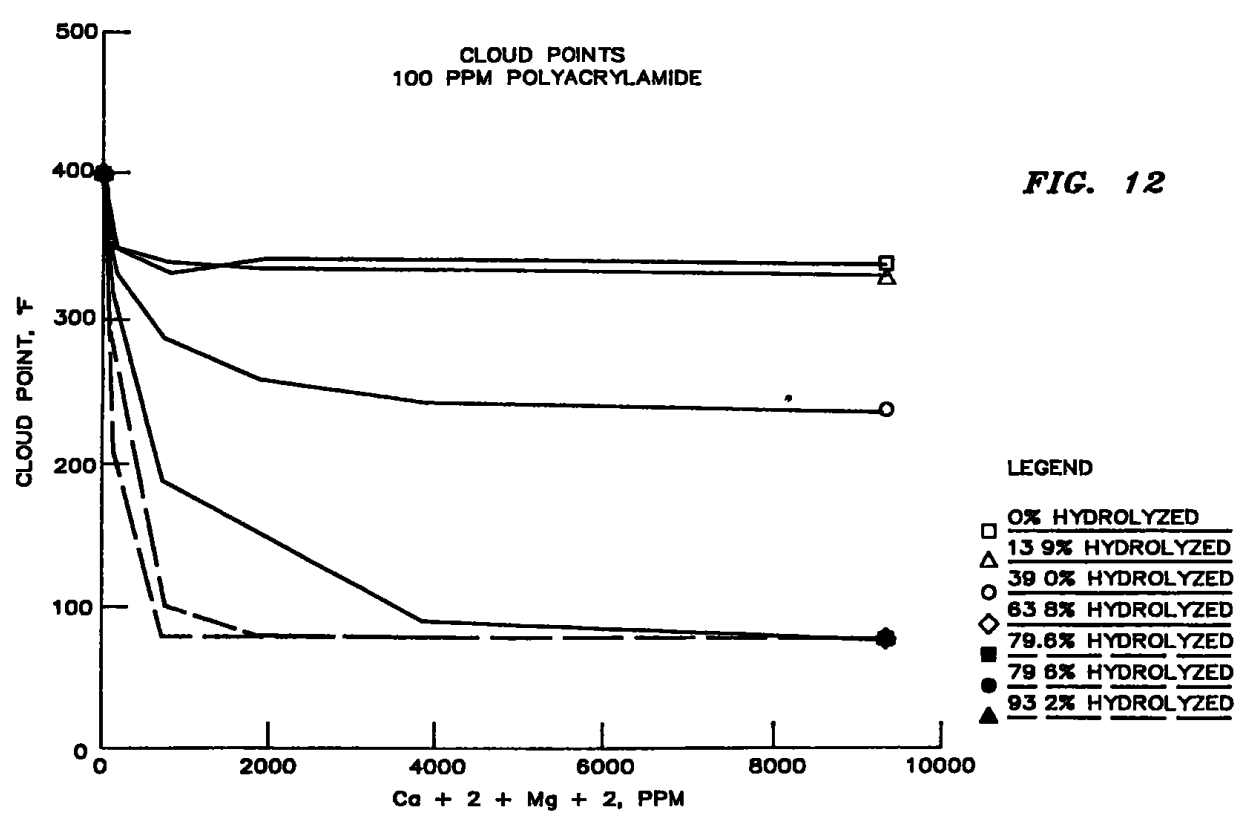


FIG. 11

90
87

88 97



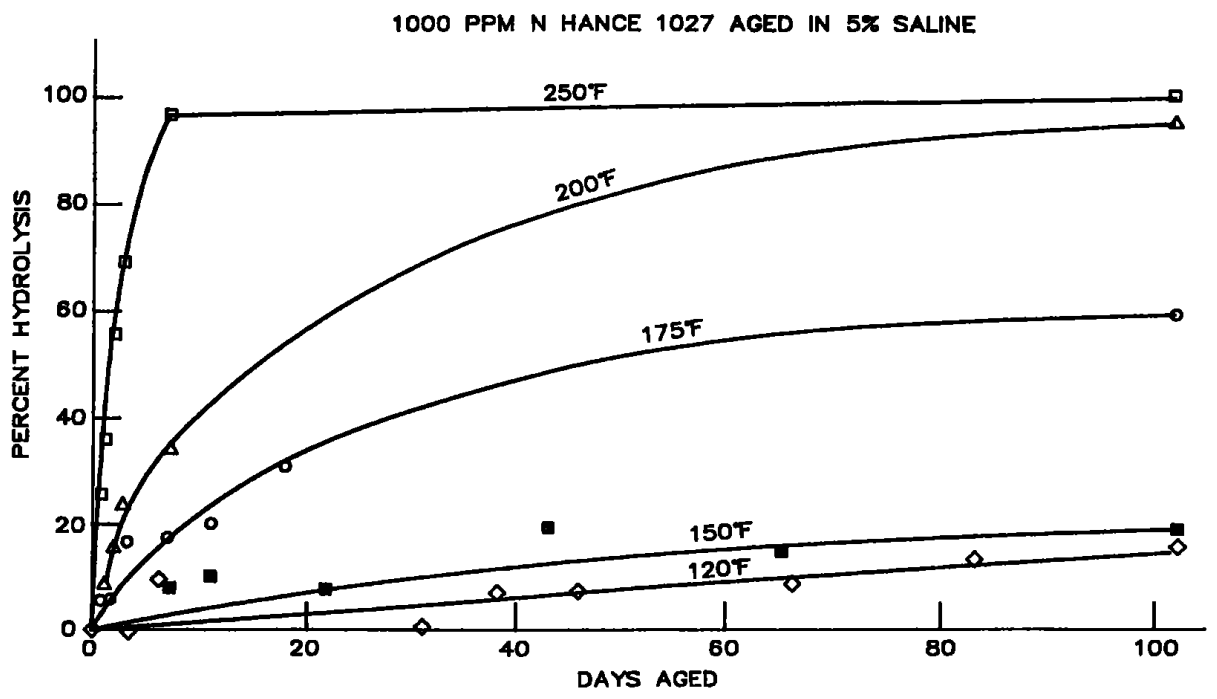


FIG. 13

92
87

93
90

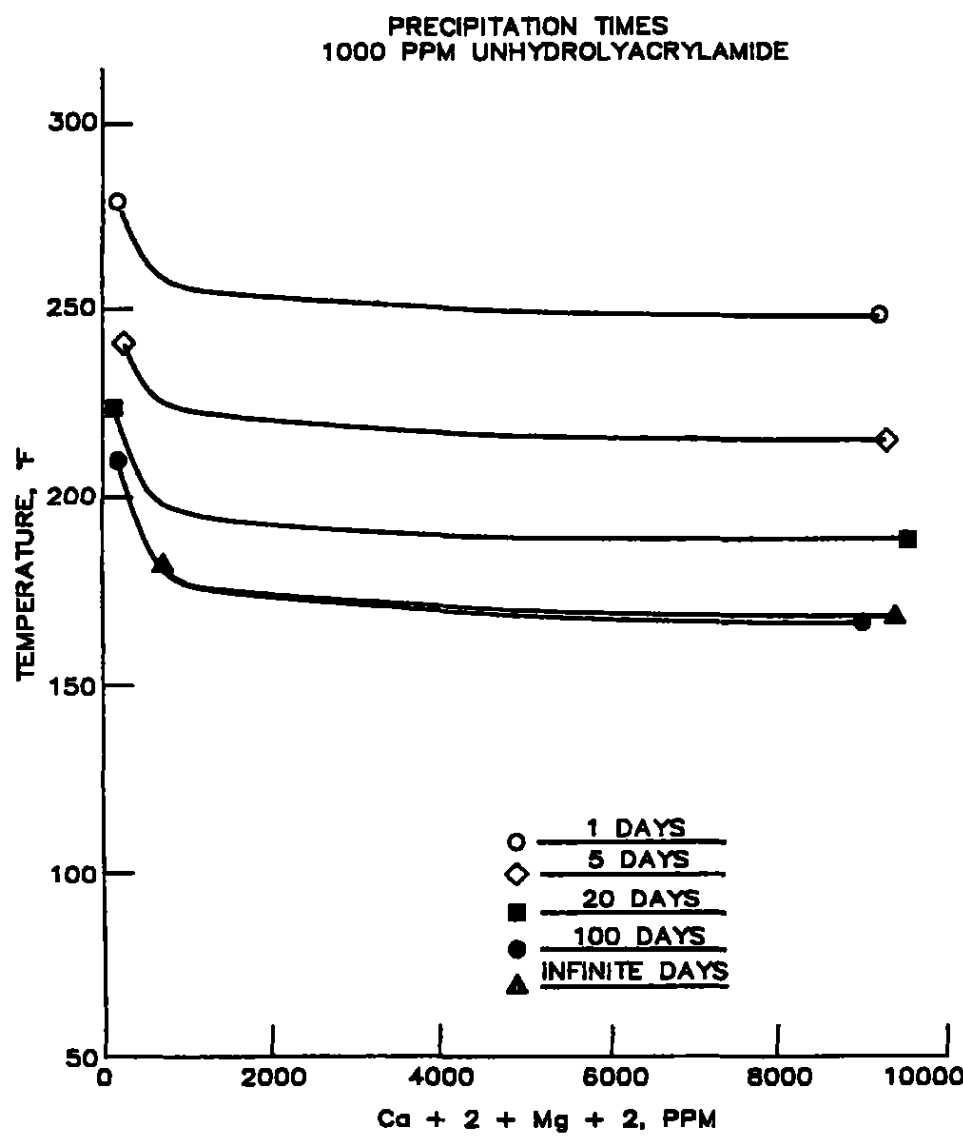


FIG. 14

95
92

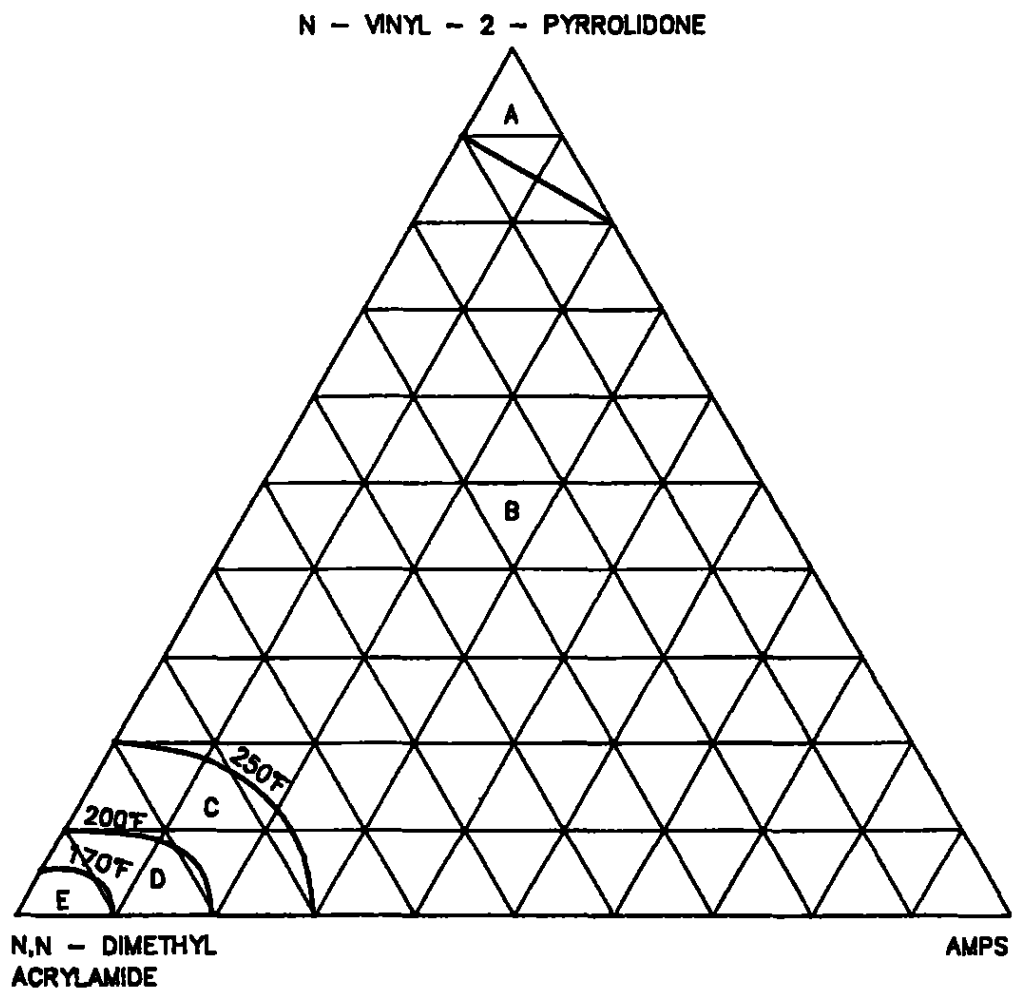


FIG. 16

POLYMERS USEFUL IN THE RECOVERY AND PROCESSING OF NATURAL RESOURCES

This application is a divisional of copending application Ser. No. 756,851 filed Jul. 18, 1985, now U.S. Pat. No. 5,080,809, which is a continuation-in-part of copending application Ser. No. 568,363 filed Jan. 9, 1984 now U.S. Pat. No. 4,951,921, which is a continuation-in-part of copending application Ser. No. 461,707, filed Jan. 28, 1983 now U.S. Pat. No. 4,644,020.

This invention relates to new and useful polymers. Further, this invention relates to the preparation of such polymers and their use in the recovery and processing of natural resources, such as for example in such applications as enhanced oil recovery, well drilling, workover and completion, the treatment and thickening of water for use in various applications, and minerals beneficiation. Still further, this invention relates to the introduction of certain polymers of the prior art as well as the inventive polymers of the present invention into subterranean well bores where high temperatures and/or salinity and/or hardness of formation waters are encountered.

BACKGROUND

Many synthetic polymers have been developed and used in processes for the recovery of natural resources. Generally a desirable property is that such polymers impart to a liquid as increased viscosity when a relatively small quantity of the polymer is added, and preferably at a minimal cost. There is an increasing demand for such polymers which will withstand hostile environments including, e.g., high temperatures, high salinity and high content of multivalent metal cations, commonly known as "hardness ions", as well as the high acidity, temperature and shear conditions encountered in processes such as acid fracturing. Various polymers may be used in the processes for recovery or treatment of natural resources disclosed below as pertinent to this invention.

ENHANCED OIL RECOVERY

Oil accumulated within a subterranean oil-bearing formation is recovered or produced therefrom through wells, called production wells, drilled into the subterranean formation. A large amount of such oil is left in the subterranean formations if produced only by primary depletion, i.e., where only formation energy is used to recover the oil. Where the initial formation energy is inadequate or has become depleted, supplemental operations, often referred to as secondary, tertiary, enhanced or post-primary recovery operations, are employed. The term "enhanced" will be used herein to refer to all such operations. In the most successful and most widely used of these operations, a fluid is injected into the formation by pumping it through one or more injection wells drilled into the formation, oil is displaced within and is moved through the formation, and is produced from one or more production wells drilled into the formation. In the particular recovery operation of this sort, field water or field brine is usually employed as the injection fluid and the operation is referred to as a waterflood. The injection water is often referred to as flooding liquid or flooding water as distinguished from the in situ formation, or connate water. Fluids injected later can be referred to as driving fluids. Although water is the most common, injection and

drive fluids can include gaseous fluids such as steam, carbon dioxide, and the like.

In one embodiment of this invention the polymers described herein are used as the polymeric viscosifier in steam stimulation. This is particularly desirable under conditions of a hostile environment. In a steamflood operation crosslinked or uncrosslinked polymeric viscosifiers in an aqueous surfactant solution and steam are injected into subterranean formations to effect permeability correction by transporting foamed surfactant into high permeability zones into divert subsequently injected steam to the relatively oil-rich less permeable zones. The polymeric viscosifier thereby greatly enhances the thermal stability of the foamed surfactant solution thus prolonging the effective time period of the permeability correction operation.

In another steam stimulation technique, the steam is injected into the reservoir followed by an extended shut in period of for instance 1-2 weeks. The steam is followed by a hot aqueous surfactant active composition. The well is put back in production immediately and any steam channelling through the surfactant causes it to foam and block the steamflow. The steam finds an alternate lower temperature zone where the heat will be transferred to the oil and formation thus providing a more efficient steam stimulation process. As the steam condenses and the foam collapses, the channels open up to produce oil. The presence of the polymers described herein (gelled or ungelled) with the steam stabilizes the foam. The foam processes to which this invention can be applied are described in U.S. Pat. No. 3,993,133, the disclosure of which is hereby incorporated by reference.

Although conventional waterflooding is effective in obtaining additional oil from oil-bearing subterranean formations, the technique does exhibit a number of shortcomings. Foremost among these shortcomings is the tendency of flooding water to "finger" through an oil-bearing formation and to thus bypass substantial portions thereof. By fingering is meant the development of unstable water stream fronts which advance toward the production wells more rapidly than the remainder of the flooding water. Furthermore, when fingering is encountered, the water does not normally displace as much oil in the portions of the formations which it contacts as it is potentially capable of displacing.

It has been established that waterfloods perform less satisfactorily with the more viscous oils than with relatively nonviscous oils. The fingering and bypassing tendencies of water are related to the ratio of the viscosity of the oil to the viscosity of the flooding water, and also related to fractures and/or high permeability zones in the formation. The viscosity of these oils varies from as low as one or two centipoise to 1,000 centipoise or higher. Water generally has a viscosity of about 1 centipoise at room temperature.

In order to restrict the mobility of the flooding water to no greater than the mobility of the oil, water thickening agents have been added to increase the viscosity of the water. Suitable agents for increasing the viscosity of the flooding water are water-soluble or water-dispersible, high molecular weight polymers. These polymers may adsorb on the formation surfaces, and accumulate in (or absorb) and reduce permeability through the rock pores. Consequently, the polymers cause the flooding water (which can contain polymer or other agents) injected therebehind to flow into previously uninvaded portions of the formation. However, these polymers are

susceptible to adverse effects present in some subterranean formations, such as high temperature and dissolved electrolytes, which cause the polymers to precipitate and/or lose their viscosity-enhancing effectiveness, thus increasing flood water mobility, and generally become less effective as mobility control agents.

To maximize the recovery of oil in post-primary oil recovery operations, a substantially uniform permeability should exist throughout the strata. If the formation permeability is heterogeneous, the flooding fluids will seek areas of high water permeability, producing channeling and the passage of excess driving fluid to the producing well. As the more water-permeable strata are depleted of oil, the driving fluid thus has a tendency to follow such channels and further increase water production, reflected in an increased water/oil ratio at the producing well. More uniform flood fronts can be obtained in formations of nonuniform permeability by permeability correction of the more water-permeable strata of the formation. One method for reducing the water permeability of these more permeable strata is the injection of plugging materials into the formation strata to at least partially plug the more water-permeable zones and achieve reduced water permeability in said zones. Plugging materials can be formed in situ in the formation by the injection of one or more reactant substances which chemically react to form bodies of reduced water permeability, alternatively monomers or prepolymers which are polymerizable under formation conditions.

DRILLING, WORKOVER AND COMPLETION FLUIDS

In the art of drilling wells to tap subterranean deposits of natural resources, such as gas, geothermal steam or oil, especially when drilling by the rotary method or the percussion method wherein cuttings must be removed from the bore hole, it is necessary to use a drilling fluid, as is well known to those skilled in the art. The subject is discussed more fully in U.S. Pat. No. 3,025,234. In addition to having the desirable rheological properties such as viscosity and gel strength, it is very important that such drilling fluids exhibit a low rate of filtration or water loss, that is, the drilling fluid must prevent excessive amounts of fluid, or "filtrate", from flowing from the bore hole into the surrounding formation. The loss of water or other fluid from the drilling fluid is prevented by the formation of a filter cake which deposits from the drilling fluid and seal the wall of the bore hole.

To produce an effective drilling mud, the clays mixed with water should disperse to a certain extent, not exceeding an acceptable operating range. That is, the individual clay particles should hydrate and repel each other and will remain in suspension (forming a "mud" or viscous drilling fluid) and filter out to form a relatively less permeable coating on the borehole walls. Excessive flocculation, however, causes larger particles to form, with the result that none of the objects of a "drilling mud" are achieved. Numerous formulations, compositions and additives to optimize the performance of drilling fluids for various applications have been developed. For instance, U.S. Pat. No. 3,816,308 discloses compositions comprising mixtures of carboxylic acid polymers and soluble metal salts with the object of increasing the "yield" (defined as the number of barrels of 15 centipose mud which can be prepared from one ton of clay) of relatively low grade bentonite clays.

High-yielding bentonite clay, when treated with high molecular weight polyacrylamide and polyacrylate polymers or copolymers of vinyl acetate and maleic anhydride, can be made to produce about the same viscosity as twice the amount of untreated bentonite. See Park et al, Oil & Gas Journal, May 30, 1960, pp 81-84.

Excessive fluid loss from the drilling fluid may contaminate the producing formation, permanently displacing oil and blocking production. If the formation penetrated is of the heaving shale type, such shale may absorb water from the drilling fluid and by a caving or swelling action, common to bentonite materials, close the bore hole around the drill stem, choke off circulation of drilling fluid, and seize the drill string. Similar results may occur simply from the abrupt increase in viscosity of the drilling fluid which is caused by excessive fluid loss. The adverse consequences of excessive fluid loss in the drilling of very deep wells are more severe due to the high temperatures and pressures encountered in such drilling operations. To increase the density of the drilling fluid so that it will exert sufficient hydrostatic pressure on the walls of the borehole, weighting agents such as heavy insoluble metal salts are added to the fluid. Drilling fluids must be of sufficient viscosity to maintain the weighting agent in suspension, but a relatively small decrease in fluid content may increase such viscosity to the point where the drill string binds. The tendency to lose liquid in a borehole is greatly increased by the high temperatures and pressures encountered.

Since most drilling fluids are "non-Newtonian" fluids, the apparent viscosity at given conditions of shear rate and shearing stress may change in a non-linear manner with certain parameters. This property makes it difficult to provide drilling fluids which will perform within acceptable ranges during the entire process of drilling a well.

In the mixing of drilling fluids in preparation for drilling operations, agitation at a certain degree of shear for some period of time is normally required to achieve the desired degree of thickening, but excessive agitation may cause the apparent viscosity to decrease. Since the degree of shear achieved in most drilling fluid circulating systems is low, it is important that a minimum of mixing time at a relatively low rate of shear produce the desired thickening, so that maximum thickening is obtained under operating conditions. Measurable variables which may characterize the apparent viscosity of a drilling fluid include the plastic viscosity, yield point and the rate and degree of gelation. The viscosity of a fluid normally decreases with an increase in temperature, but certain polymer additives or deflocculating agents may reduce, or even reverse, this tendency. However, the long-chain polymers which are most effective in achieving this effect are the most vulnerable to breakdown through oxidation, shear and thermal effects, i.e. the duration of exposure to high temperature drilling operations. Also, many such polymers tend to precipitate and/or lose viscosity as well as effectiveness as water loss additives when exposed to dissolved electrolytes, particularly when divalent metal cations such as Ca^{++} and Mg^{++} are present. In drilling fluids, the resulting vulnerability to breakdown is exacerbated by the density of the mud, which is directly related to the weighting agents required for a given formation pressure. The extremely high temperatures encountered in

drilling geothermal wells also tend to cause early breakdown of mud additives.

Breakdown of water loss control polymers or defloculants causes a large increase in the fluid loss accompanied by an increase in filter cake thickness. The thickness of filter cake will be determined by the solids content of the mud. High density drilling fluids with large amounts of weighting materials produce very thick filter cakes when fluid loss control is lost. These conditions often result in differential sticking of the drill string. It is desirable to develop additives which will enable drilling fluids to retain their proper viscosity and fluid content over a broader range of conditions.

Drilling fluids are used in the drilling of various types of wells. Workover and completion fluids, in contrast, are those fluids used in the completion and servicing of such wells. Completion fluids are those fluids used after drilling is complete and during the steps of completion, or recompletion, of the well. Completion can include cementing the casing, perforating the casing, setting the tubing and pump, etc.

Workover fluids are those fluids used during remedial work in the well. This can include removing tubing, replacing a pump, cleaning out sand and other deposits, logging, re-perforating, etc.

Further with regard to sand consolidation, the polymers described herein are particularly useful because of their stability under hostile environment conditions. Sand consolidation is broadly disclosed in U.S. Pat. No. 3,978,928 the disclosure of which is hereby incorporated by reference. The in situ gelation of the polymeric viscosifier can involve crosslinking through the use of polyvalent metal ions such as aluminum or chromium or a sequestered metal system such as aluminum citrate, as described in detail herein.

In one embodiment of this invention the polymers disclosed can be used as thickening agents in hydraulic fracturing processes of the type described, for instance, in U.S. Pat. No. 3,727,689 the disclosure of which is hereby incorporated by reference. The use of polymeric viscosifiers comprising N-vinyl-2-pyrrolidone copolymers such as 50/50 wt/wt poly (N-vinyl-2-pyrrolidone-co-acrylamide) imparts excellent thermal stability to sand fracturing fluids even in the presence of hard brines and high temperature, i.e. hostile environments. Other ratios of monomers can also be used, generally from 70:30 to 30:70 weight percent poly(N-vinyl-2-pyrrolidone acrylamide). Polyvalent metal crosslinking of sand copolymers can be effected by a redox couple e.g., sodium dichromate/sodium bisulfite or with aluminum cation sequestered with citrate as further described herein.

In one embodiment, this invention is used in fracture plugging of subterranean formations as disclosed in U.S. Pat. No. 3,845,822 the disclosure of which is hereby incorporated by reference. In a fracture plugging process the in situ polyvalent metal crosslinking of the polymeric viscosifiers is triggered by the sequential injection of (1) an oxidant composition containing a reducible polyvalent metal such as chromium +6 as sodium dichromate and (2) a water-soluble sulfur-containing reducing agent such as sodium bisulfite (redox system). The stability to hostile environment conditions of the polymers described herein make them particularly suited to use in fracture plugging.

Workover also broadly includes steps used in preparing an existing well for secondary or tertiary oil recovery

such as polymer additions, micellar flooding, steam injection, etc.

Both workover and completion fluids are used in part to control well pressure, to prevent the collapse of casing from overpressure, and to prevent or reduce corrosion of casing. A drilling fluid may be suitable for completion or workover applications in some cases, but not in all cases. When a special workover or completion fluid is used, it is usually a poor or unsuitable drilling fluid.

The compositions of workover and completion fluids can differ from the compositions of drilling fluids, since workover and completion fluids have functions which differ from those of drilling fluids. A workover or completion fluid differs from a drilling fluid in several ways. A workover fluid does not have to be compatible with drilled solids. Usually, a workover fluid is used in cased holes, and the formation is exposed only at perforations. Whereas a drilling fluid must protect the formation from swelling or disintegration, a workover fluid must not damage the permeability of the formation. Ideally, a workover fluid would contain no solids. If solids must be used, they should be acid soluble. Similarly, the compositions, properties and functions of workover fluids can differ from those of completion fluids.

Although there has been considerable progress in the field of workover and completion fluids, there is significant room for further improvement. For example, wells are being completed and serviced in increasingly hostile environments involving, e.g., high temperatures and high levels of salinity and/or hardness in the formation water. Thus, new additives for workover and completion fluids which retain their properties at elevated temperatures and high concentrations of dissolved electrolytes are in demand.

TREATMENT OF MINERALS AND WATER

In processing mineral ores it is often necessary to separate finely divided solids from aqueous suspension, conversely, in treating water for use, e.g., for municipal water supplies or industrial applications, it is often necessary to remove finely divided solids which may be suspended therein. Improvements in the ease of separation of finely divided solids from aqueous suspensions either by sedimentation or by filtration have been accomplished by incorporating small amounts of high molecular weight water-soluble polymers in such suspensions. Among such polymers high molecular weight polyacrylamide and hydrolysis products thereof have proven to be effective on a wide variety of ore suspensions. Improved polymers have been developed for this purpose, for example, Sullivan discloses in U.S. Pat. No. 3,146,193 (1964) certain high molecular weight water-soluble copolymers of certain vinyl substituted, nitrogen-containing, heterocyclic ring compounds with acrylamide which can be incorporated in aqueous suspensions of finely divided inorganic solids to facilitate the concentration and separation of such solids.

Further improved polymers are in demand for applications involving concentrated brine solutions, e.g., potash ore processing. The American potash industry annually treats more than 18 MM tons of ore from which more than 3 MM tons of potash concentrate is recovered. Most of this product is used as fertilizer; however, nearly all of the potassium required by other U.S. industries comes from this concentrate.

A typical potash ore consists of sylvite (20-25%), halite (60-75%), and clay (4-20%). The potassium con-

taining mineral is sylvite (KCl). The major impurities are halite (NaCl) and clay. The mixed ore is processed at the mine site. The processing varies with the level of clay, the higher clay ores requiring a more extensive treatment. This extensive treatment is becoming more widely utilized as the mines grow more mature and use lower grade ores.

The adverse effect of clay is caused by the high affinity of potash collectors for clay, which diminishes their cost effectiveness. In the processing, which consists of subsequent crushing, grinding, hydrolytic clay removal, and flotation, the time, cost and steps required depend upon the clay content. When more than a few percent of clay is present, the clay must be "blinded" by polyacrylamide, guar gum, or potato starch before collector addition.

A preferred step would be clay removal by flocculation with a brine soluble polymer, since all processing is conducted in saturated brine to prevent mineral dissolution. This polymer, in addition to brine solubility, must retain its activity and thus cost effectiveness in the presence of the high ionic strength brine medium. The effectiveness of most polymers, such as the polyacrylamides, are reduced, and in many cases the polymers are actually precipitated in such brines. Thus, effective flocculating agents which will withstand such saturated brines are in demand.

POLYMER ADDITIVES

In some cases, various polymers have been found useful in more than one application, such as those described above. However, among the most severe applications is enhanced oil recovery, in which polymer additives must form stable and viscous aqueous solutions while exposed to high temperatures and dissolved electrolytes for as long as several years, often requiring retention of a solution viscosity of at least about 10 centipoises at room temperature, and must reduce the permeability of rock to the flooding water by adsorbing on the rock in the formation. Many commercial water-soluble polymers have been tested for applicability in enhanced oil recovery, but prior to the present invention no such polymer has fully satisfied the requirements referred to above.

Polyacrylamide, for example, provides the desired viscosity and reduces rock permeability in many instances, but it frequently loses viscosity in water containing dissolved electrolytes. Polyvinylpyrrolidone, although stable in the presence of dissolved electrolytes including multivalent cations at the temperatures high enough to cause hydrolysis of polyacrylamide at significant rates (i.e., <200° F.), has only been available in grades of low viscosity. Polyvinylpyrrolidone also demonstrates undesirable adsorption on rock, thus an undesirable resistance factor and residual resistance factor. Furthermore, polyvinylpyrrolidone is much more expensive than polyacrylamide and many other commercial polymers. Thus, it is apparent that as the demand for recovery and processing of natural resources increases, improved polymer additives for such processes as enhanced oil recovery will be in demand. See, e.g., Davison and Mentzer, "Polymer Flooding in North Seal Oil reservoir," paper SPE 9300, presented at Fall Conference of Society of Petroleum Engineers of AIME, Dallas, Tx., Sept. 21-24, 1980 and published in the Society of Petroleum Engineers Journal, June 1982, pp. 353-62. Davison and Mentzer evaluated over 140 polymers (generally classified as polyacrylamides,

polyvinylpyrrolidone, hydroxyethyl celluloses, cellulose sulphate esters, guar gums, xanthans and scleroglucans) for viscosity retention and porous media flow performance under high temperature (90° C., 194° F.), high salinity, and high pressure conditions. For polymer flooding in North Seal oil reservoirs, the criteria were that a polymer solution should be five times more viscous than sea water and lose less than 20 percent of its viscosity in 500 days at 90° C. Scleroglucan polymers gave the best performance in the tests, producing the required viscosity in polymer solutions of about 500 ppm and retaining most of this viscosity through 500 days' aging at 90° C. Polyacrylamides were "particularly unsuitable", as they precipitated within 60 days in 90° C. seawater, apparently due to the presence of calcium and magnesium ions. Polyvinylpyrrolidones were very stable but had to be used in high concentrations (20,000 ppm) to give adequate viscosity. There is no indication that copolymers of vinylpyrrolidones and acrylamides were tested at high temperatures. McCormick et al DOE/BETC/3603-10, p. 5, 117 prepared such copolymers but concluded that they had "low solution viscosity and appear of little value in EOR." Thus they were not tested. Thus, there is a substantial need for polymers which would be useful in the recovery of natural resources in hostile environments, such as in North Seal oil reservoirs, and in various operations for processing natural resources in hostile environments.

SUMMARY OF THE INVENTION

Among the objects of the invention are polymers suitable for use in the recovery and processing of natural resources, such as in enhanced oil recovery operations, in drilling, workover, and completion fluids, and in the treatment of minerals and water. Other objects of the invention are polymers suitable for use in subterranean well bores and reservoirs, such as oil-bearing reservoirs, and in the treatment of minerals and water when the polymers are exposed to severe conditions, including high temperatures and/or highly saline environments and/or water with a high concentration of hardness ions.

Other objects of the invention are processes for the recovery and processing of natural resources as described above. Further objects of the invention are processes for the recovery and processing of natural resources in which polymers are employed that are suitable for exposure to severe conditions as described above.

Other objects, advantages and features of the invention will be readily apparent to one skilled in the art from the following detailed description of the invention, the drawings, and the appended claims.

According to this invention, novel processes are provided comprising the introduction of polymers comprising an N-vinyl lactam and an unsaturated amide into a subterranean well bore, such that said polymers are exposed to hostile conditions such as temperatures of at least about 120° F. Said polymers are stable when exposed to water of significant salinity and/or hardness. The polymers can be at least partially dissolved in various fluids, including for example an aqueous fluid, or in a fluid containing at least one component selected from the group consisting of bases, polymeric viscosifiers, surfactants and cosurfactants, and combinations of any two or more of said components. The polymers can be crosslinked with various crosslinking agents.

The polymers are preferably water-soluble or water-dispersible.

Further according to this invention, novel methods are provided for the preparation of novel polymers of N-vinyl lactams, preferably N-vinyl-2-pyrrolidone, including homopolymers, copolymers and terpolymers. In one embodiment of the invention, such polymers are prepared using particular polymerization media and polymerization initiators or radiation sources, which produce polymers useful in the recovery and processing of natural resources, such as introducing such polymers into a subterranean well bore as above described. When the polymers are prepared in preferred polymerization media such as water containing mixed electrolytes with a free radical initiator, novel polymers are obtained which have relatively high viscosity and molecular weight, and maintain these properties even in harsh environments having high temperature and/or salinity and/or hardness. Also according to the invention, a polymerization medium consisting essentially of a tertiary alcohol and a free radical initiator can be employed.

Further according to this invention, novel methods are provided for the production of terpolymers, consisting essentially of the comonomers as described above polymerized with a minor amount of a termonomer of a hydrophobic or non-ionic character.

When these copolymers and terpolymers are prepared by combining the monomer units in certain preferred proportions in preferred polymerization media such as water containing mixed electrolytes, or a neat tertiary alcohol such as t-butyl alcohol, with a free radical initiator selected from certain organic azo compounds or organic peroxides, or using electromagnetic radiation such as gamma radiation, polymers are obtained which have high viscosity and molecular weight and which maintain their viscosity, thus their usefulness, even in harsh environments having high temperature, salinity and/or hardness, and when subjected to shear conditions. Certain of these polymers can be characterized by K values of greater than 140 (K values are related to relative viscosity, as discussed fully herein.) By using slightly different proportions of monomer units and different molecular weights in some cases, it has been discovered that the resulting copolymers and terpolymers are generally useful in processes for the recovery and processing of natural resources comprising enhanced oil recovery, use as additives for driving, workover and completion fluids, selective plugging of zones of excess permeability in subterranean formations by in-situ polymerization, the treatment of minerals in their recovery and processing, flocculation of suspended solids, and the thickening and treatment of water for various uses.

Further in accordance with this invention, it has been discovered that polymers of superior properties can be prepared by a method of polymerizing a monomer mixture comprising N-vinyl pyrrolidone and acrylamide employing electromagnetic or nuclear radiation, preferably in an aqueous polymerization medium.

Furthermore, it has been discovered that in processes comprising the introduction of a polymer into a subterranean well bore so that said polymer is exposed to a temperature of at least about 120 F., especially in waters of high salinity and/or hardness, the copolymers and terpolymers of the prior art comprising monomers and termonomers as described herein can be used as well as the inventive analogous polymers prepared by the

methods of this invention in the specified polymerization media. Further advantages are apparent when such polymers are exposed to temperatures of at least about 150 F., particularly for temperatures above about 200 F., including temperatures of 250 F., 275 F., and even 300 F.

Further in accordance with the present invention, polymers prepared in accordance with this invention are added to a liquid containing solids to aid in flocculating such solids, wherein the temperature of the liquid is at least about 130 F. and/or the liquid has a salinity of at least about 10 grams per kilogram of solution.

In accordance with one process of this invention, a polymerization inhibitor is introduced into an oil-bearing formation under conditions designed to allow permeation of the polymerization inhibitor into both the more permeable zones and the less permeable zones, followed by a flush which selectively removes the polymerization inhibitor for the more permeable zones. After this, a mixture of N-vinyl lactam, unsaturated amide and optionally, a minor portion of a termonomer, and a polymerization catalyst are introduced into said formation together or independently to form a fluid diversion plug in the absence of the polymerization inhibitor, thus selectively plugging the more permeable zones in the formation. The preferred monomers of this invention polymerize well in polymerization media similar to the connate water found in the oil-bearing formations, and the polymers thus formed in situ retain their viscosity well under the conditions encountered in "hostile" formation environments, e.g. high temperature, high salinity and/or high concentration of hardness ions.

Still further according to this invention polymer compositions of at least one of a hydrophilic N-vinyl lactam and a hydrophilic vinyl-containing sulfonate and optionally an unsaturated amide are used to thicken water used to recover oil under hostile conditions.

Still yet further in accordance with this invention a polymer which is not capable of imparting as high a viscosity to water as a polyacrylamide is used under hostile environment conditions where acrylamide polymers are useless because of precipitation.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG 1 shows the variation of viscosity with temperature of unaged polymers of this invention compared with polymers of the prior art and synthetic sea water.

FIG 2 shows the variation of viscosity with temperature of heat-aged polymers of FIG 1.

FIG 3 illustrates the viscosity ratio of aged copolymers of the invention as a function of comonomer proportions.

FIG 4 illustrates cloud point temperatures for copolymers of the invention aged at different temperatures.

FIG 5 illustrates equilibrium cloud point temperatures for copolymers of the invention aged at different temperatures.

FIGS 6 and 7 illustrate the degree of hydrolysis of the acrylamide units attained in copolymers of the invention aged at different temperatures.

FIG 8 shows K values for copolymers of the invention at various concentrations compared with copolymers of the prior art.

FIG 9 shows K values for copolymers of the invention as well as copolymers of the prior art at various

concentrations and for various polymerization and test media

FIG 10 illustrates Screen Factors for copolymers of the invention tested at various concentrations in SSW

FIG 11 illustrates the viscosity of homopolymers of this invention which are subjected to heat aging.

FIG 12 is a plot of cloud point versus multivalent cation concentration

FIG 13 is a plot of per cent hydrolysis versus days aged

FIG 14 is a plot of precipitation times as a function of temperature and divalent ion concentration.

FIG 15 is a plot of aged viscosity data on polymers having monomer ratios of components as shown on the triangular graph.

FIG 16 is a plot similar to FIG 15 except the unsaturated amide is N,N-dimethylacrylamide

DETAILED DESCRIPTION OF THE INVENTION

Polymers

As used herein the term "polymers" is used generically, unless otherwise indicated, to mean homopolymers, copolymers and terpolymers and thus includes polymers prepared using any number of monomers.

The homopolymers of N-vinyl lactams prepared in accordance with this invention have improved viscosity, and maintain this viscosity well under adverse conditions such as high temperature, high salinity and/or high concentrations of "hardness" ions. Thus, despite their relatively high cost compared to some commercial polymeric viscosifiers, these polymers are suitable for certain processes for the recovery of natural resources under such adverse conditions.

The copolymers and terpolymers of this invention appear to be well suited for various applications including enhanced oil recovery (EOR), drilling fluid water loss additives, workover and completion fluid additives, selective plugging of "thief zones", minerals beneficiation, water thickening, water treatment, and the like. In a presently preferred embodiment, the copolymers and terpolymers, to be described subsequently, are well adapted because of their outstanding viscosity stability in hostile, saline, hard water environments, for polymer-flooding purposes. A hostile environment for the purpose of this application is one in which the temperature, salinity and/or hardness cation content is high enough to cause precipitation, loss of viscosity and/or similar adverse effects within a nominal period of time in conventional polymers otherwise suitable for use in such applications. Such conventional polymers include, for example, polyacrylamides. The advantages of the polymers of this invention are apparent when they are employed in hostile environments of at least 120° F or as more specifically defined in FIG 14. Brackish and/or hard aqueous fluids having a salinity of at least about 10 grams per kilogram of solution and/or a fraction of divalent hardness ions to total cations of at least about 1 weight percent and particularly at least about 5 weight percent in combination with temperatures of at least about 120° F are considered hostile environments. Since hardness cations such as Ca^{+2} and Mg^{+2} are particularly damaging to many such polymers, when the salinity and hardness cation content are relatively high the hostile zone is defined by a relatively lower temperature. A hostile environment, for example, is one wherein the reservoir temperature can be as low as 150° F and the electrolyte concentration of dissolved salts in

the available water, both injection water (which may be seawater) and formation water, is at least about 35,000 ppm (with about 1750 ppm combined calcium and magnesium ions), i.e., about 3.5 weight percent or higher, equivalent to a salinity of about 35 grams per kilogram of solution. At lower reservoir temperatures, from e.g. about 120° F up to about 150° F, a relatively higher salinity and/or content of hardness cations would create such a hostile environment, say, for example a salinity of at least about 50-100 grams per kilogram with a fraction of divalent hardness cations to total cations of at least about 20 weight percent. At temperatures of at least about 120° F, a hostile environment for polymeric viscosifiers can also be created by a strongly basic environment, e.g., concentrations of at least about 5 weight percent to of strong base, which accelerates the hydrolysis process in many polymers. Such conditions are encountered in processes comprising, e.g., caustic flooding of oil-bearing subterranean formations.

A hostile environment can best be viewed as one in which conventionally used thickening agents are unstable. Polyacrylamides are such conventionally used thickening agents.

Polyacrylamides as commonly used for Enhanced Oil recovery (EOR) hydrolyze at elevated temperatures and will eventually precipitate in the presence of divalent cations. The following is the method by which the limits of a hostile environment are determined using this criteria. That is, the boundary below which this polymer remains in solution indefinitely and above which in days or months it falls out of solution, resulting in loss of polymer viscosity and plugging of the formation defines a hostile environment.

Any polyacrylamide in hard brines will eventually turn cloudy (i.e., begin to precipitate if its temperature is raised high enough). FIG 12 shows the cloud point as a function of divalent cation concentration for 1000 ppm by weight originally unhydrolyzed commercial polyacrylamide in various brines. These solutions were thermally hydrolyzed to different levels in 5% saline solution prior to addition of divalent cations (equal amounts of calcium and magnesium in ppm by weight) and making cloud point measurements. In the absence of divalent cations (a condition not found in petroleum reservoirs), this polymer stays in solution up to 400° F (the limits of the measurement) regardless of the level of hydrolysis. The presence of divalent cations, on the other hand, affects the cloud point depending on the hydrolysis and hardness level. That is, the higher the hydrolysis level and divalent cation concentration, the lower the cloud point.

FIG 13 shows the effects of time and temperature on the hydrolysis of 1000 ppm of the same unhydrolyzed commercial polymer. This figure indicates that at a given temperature the level of hydrolysis increases with time, but eventually reaches an equilibrium. Using a standard thermodynamic treatment of an equilibrium reaction, where K_{eq} is the equilibrium constant, ΔS° and ΔH° are the standard entropy and enthalpy changes for the reaction, R is the gas constant and T is the absolute temperature

$$\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (1)$$

Fitting this equation to K_{eq} and T values derived from FIG 13 gave values of ΔS° and ΔH° , which were then

used to calculate K_{eq} and equilibrium level of hydrolysis for any desired temperature. A standard analysis of the kinetics of hydrolysis gives the following equation

$$\frac{A_0 - A_t}{A_0 + A_t} \ln \frac{A_0^2 - A_t A_e}{(A_0 - A_t) A_e} = k_f t \quad (2)$$

where A_0 , A_e and A are the amide concentrations at zero time, at equilibrium and at t , respectively, and k_f is the rate constant for the forward (hydrolysis) reaction. By fitting amide concentrations to equation (2) k_f values were calculated for the five temperatures represented in FIG 13. A fit of these results to the Arrhenius equation

$$k_f = C e^{-E_a/RT} \quad (3)$$

gave values for C , the pre-exponential factor and E_a , the activation energy. The forward rate constant for any desired temperature could then be calculated. Using the k_f value for a given temperature and equation (2), the time required to achieve a given degree of hydrolysis can be calculated. This can be done so long as the desired hydrolysis level is lower than the equilibrium level of hydrolysis for that temperature, that is as long as $A > A_e$ in equation (2). For $A = A_e$ this equation predicts time to approach infinity, and for $A < A_e$ time is undefined. In other words the hydrolysis level at any temperature cannot exceed the equilibrium value for that temperature.

FIG 12, with appropriate interpolation, can be used to define the hydrolysis level that causes the onset of precipitation for any given temperature and hardness level. Equations (1), (2), and (3) predict the time taken to reach this level of hydrolysis. If the equilibrium hydrolysis level is less than the level causing instability, the time is infinite. In other words, an initially unhydrolyzed polyacrylamide will be indefinitely stable under the chosen conditions. If the equilibrium hydrolysis level is greater than the level causing instability, the polymer will ultimately precipitate and the calculation gives the time to the onset of instability. If the two hydrolysis levels are exactly equal, the stability limit has been defined.

By repeated calculations at closely spaced temperatures for many hydrolysis levels, FIG 14 was generated. This gives contour lines of equal precipitation time as a function of temperature and hardness level. Any conditions above and to the right of the infinity line represent hostile environments for polyacrylamides in the sense that the polymer will eventually precipitate. Note that the 100 days line lies very close to the infinity line, indicating that within a practical range of times for EOR projects the actual stability time is not much of an issue.

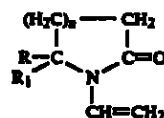
It must be pointed out that FIG 14 is for an unhydrolyzed polymer and the stability times represented are much longer than for already partially hydrolyzed (~30%), polyacrylamides commonly used in EOR. Furthermore, the polymer used in this study has a moderate molecular weight (MW) and those commonly used in EOR with higher MW will precipitate at lower temperatures under the same hardness and hydrolysis levels. It must also be mentioned that polymer concentration may play a role in precipitation of polymer and FIG 14 represents stability limits for 1000 ppm of polymer.

Since there is so little difference between the 100 day curve and the infinity curve, there is no need to make an arbitrary designation of a time limit for the time parameter but rather infinity can be used. Also, since almost all formations where there is an otherwise hostile environment will have at least 400 to 1000 ppm multivalent cations, and since the infinity curve becomes almost flat after about 1000 ppm, the hardness parameter can simply be anything greater than 500-1000 ppm by weight multivalent cations. This leaves the temperature as the significant factor, the temperature being anything over about 170° F at greater than 1000 ppm multivalent cations although, of course, defining the hostile environment as above (i.e. above and to the right) of the infinity line is more precise. Generally the temperature will be within the range of 170°-400° F or at least 170°-300° F and the multivalent cation concentration will be within the range of 500 to 220,000 or more likely 1000 to 10,000 ppm by weight based on the weight of water.

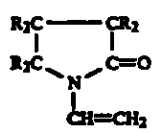
Although several biopolymers have been reported to be stable in sea water for extended periods at temperatures up to a range of from about 150 F to nearly 200 F, above about 200 F the only water-soluble polymer known to maintain its solution viscosity under these conditions is polyvinylpyrrolidone (PVP). However, PVP is relatively expensive and it requires high concentrations, e.g. about 20 weight percent or more, to obtain suitable viscosities for polymer flooding.

The copolymers and terpolymers of this invention are generally water-soluble or water-dispersible and cheaper to prepare than PVP. These polymers can be retained in solution in the aqueous polymerization medium in which they are prepared. When prepared by radiation polymerization in a viscous polymer mass (commonly known as a "gel log") the polymers are also water-soluble. However, when the polymer is separated from such an aqueous medium and dried, it is generally expected to be water-dispersible and/or swellable, but may not be completely water-soluble. On the other hand, the polymers separated from a polymerization medium consisting essentially of a tertiary alcohol in accordance with this invention and dried appear to be generally water-soluble, which can be an advantage when a granular, water-soluble polymer material is desired. They have been found to provide adequate solution viscosity with exceptional thermal stability and resistance to electrolyte effects, thus are superior to PVP for EOR in hot, saline environments, especially those containing "hardness" or multivalent metal cations such as Ca^{+2} , Mg^{+2} , etc. Their preparation and properties are described in Examples I, II, III, IV, V, VI, VII, VIII, XIV, XV, XVI, XVII, XVIII, XIX, XX, XXI, and XXII.

The polymers of this invention are derived from monomer units of N-vinyl lactams preferably having the formula

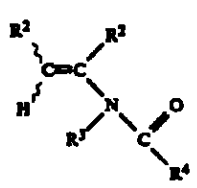


where R and R_1 are selected independently from the group consisting of hydrogen, methyl and ethyl and n is an integer of from 1 to 3. These monomers are generally water-soluble or water-dispersible. A more preferred class of compounds are those of the formula



where R is hydrogen, methyl or ethyl. The monomer unit presently most preferred is N-vinyl-2-pyrrolidone. Preparation and properties of the homopolymers are described in Examples XI and XII.

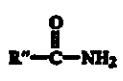
Alternatively, in place of or in addition to the N-vinyl lactams, i.e., N-vinyl cyclic amides, open chain N-vinyl amides suitable for use in the present invention are described by the formula



wherein each R² is independently selected from H and 1-6 preferably 1-2 carbon atom alkyl groups, R³ and R⁴ are selected from 1-3 carbon atom alkyl groups. The preferred monomer is N-methyl-N-vinylacetamide because of the exceptional resistance to hydrolysis of copolymers made therewith in combination with the unsaturated amide monomers and/or vinyl-containing sulfonate monomers described herein. Such polymers are particularly suited for reservoirs of 190 F or greater (88° C.) in the presence of 400 or more ppm multivalent cations such as Ca⁺² or Mg⁺².

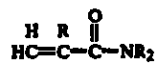
Although the R², R³, and R⁴ groups can be independently selected as noted, the resulting monomer must be hydrophilic as defined herein to be used as the N-vinyl amide component of compositions of this invention. These alternative N-vinyl amide components can be viewed as open chain or with the R³ and R⁴ groups fused as the lactam component. Hence the generic term N-vinyl amide is used to include both the lactam and the open chain N-vinyl amide, these both being hydrophilic.

Copolymers of this invention are produced by copolymerizing a comonomer of an unsaturated amide having the formula



where R'' is an unsaturated radical selected from 1-alkenyl groups such as ethenyl (vinyl), propenyl, isopropenyl, 1-butenyl, isobutenyl (2-methyl-1-propenyl), 1-pentenyl, 1-isopentenyl (3-methyl-1-butenyl), and 1-methyl-1-butenyl with a comonomer of at least one N-vinyl lactam as described above. These unsaturated amides are generally water-soluble or water-dispersible. The monomers presently preferred are N-vinyl-2-pyrrolidone (VP) and acrylamide (Am). For convenience, the terms VP and Am will be used to refer to the first and second monomers, respectively, in the discussions herein.

A more preferred class of unsaturated amide monomers are those of the formula



wherein each R' is individually selected from H and methyl. Especially suitable in addition to acrylamide are N-methylacrylamide and N,N-dimethylacrylamide (DMAm). For both the vinyl lactam and unsaturated amide the scope can be viewed functionally as including the replacement of hydrogens with hydrocarbon groups so long as the monomer remains hydrophilic. By hydrophilic is meant if the monomer were homopolymerized, the polymer would be water soluble. A monomer which may not form a water-soluble homopolymer but which, in the amount used in a copolymer results in a water-soluble copolymer is also viewed in a broader sense within the definition of hydrophilic.

The minimum amount of N-vinyl lactam comonomer required is that amount necessary to provide the desired polymer properties, e.g. viscosity and stability, under the expected environmental conditions. For example, polymers containing a minor amount, up to about 10 weight percent, of the vinyl lactam could be effective in the recovery and processing of natural resources, such as for example in enhanced oil recovery in reservoirs having temperatures in the range of about 120 F to about 150 F and/or formation waters of significant salinity and/or hardness. Polymers of these proportions could also be useful under more adverse conditions if exposed for shorter periods of time.

The monomer weight ratios of the copolymers can vary rather widely. Generally, VP:Am ratios in the range from about 10:90 to about 90:10 are employed depending upon the intended application, but preferably VP:Am weight ratios in the range of about 25:75 to about 75:25 are employed, more preferably from about 40:60 to about 70:30. The optimum VP:Am weight may vary according to the application. For example, in EOR the range presently preferred is from about 65:35 to about 50:50, based on prolonged aging studies conducted with the copolymers, but for in situ polymerization applications a relatively broad range of from 25:75 to 75:25 is preferred. A copolymer presently particularly preferred for certain applications after heat aging at 250 F contains about 60 weight percent VP and about 40 weight percent Am, corresponding to a 1:1 molar ratio. The VP:Am weight ratios of 10:90 to 90:10 correspond to molar ratios of about 6:94 to 85:15.

After heat aging, copolymers of these 60:40 proportions have been found to retain their viscosity well in hot, saline environments. On the other hand, when the copolymers are to be used without such pre-aging, higher, if less persistent, viscosities have been obtained with copolymers having VP:Am weight ratios in the range of from about 45:55 to about 55:45, or preferably about 50:50. Since the VP:Am weight ratios are expressed in terms of 100 parts by weight of the copolymer, the weight percentages of the monomer units in the copolymer can be read directly.

Further in accordance with this invention, novel and useful terpolymers can be prepared by copolymerizing a first monomer unit of an N-vinyl lactam and a second monomer unit of an unsaturated amide as described above with a minor portion of a third monomer selected from the group consisting of hydrophobic compounds, vinyl pyridines and hydroxyalkyl esters of ethylenically-unsaturated carboxylic acids and combinations of

any two or more thereof. Particularly suitable second monomers are acrylamide and N-substituted unsaturated amides such as N,N-dimethylacrylamide. For convenience, the third monomer will hereinafter be referred to as a termonomer, as distinguished from the first and second monomer units described above, which are referred to as comonomers, or VP and Am for convenience. The hydrophobic compounds suitable for the termonomers are generally selected from the group consisting of monovinyl aromatic hydrocarbons having from 8 to about 12 carbon atoms such as styrene, vinyl esters of saturated carboxylic acids having from 3 to about 6 total carbon atoms such as vinyl acetate, alkyl esters of ethylenically-unsaturated monocarboxylic acids having from 3 to about 22 carbon atoms, such as ethyl acrylate, and ethylenically-unsaturated nitriles having from 3 to about 5 total carbon atoms, such as acrylonitrile. Other suitable hydrophobic monomers are N-vinyl acetamide and 2-vinyl quinoline. Also suitable hydrophobic monomers are acryloyl pyrrolidones, diacetoneacrylamide and N- and N,N-alkylacrylamides where the alkyl groups contain more than two carbon atoms. By hydrophobic is meant that if the monomer were homopolymerized it would be water insoluble although in amounts up to 25 percent it can be present herein and the total polymer is still water soluble. Other suitable compounds (hydrophilic but not anionic) include vinyl pyridines such as 4-vinyl pyridine, acryloyl morpholine, methyl vinyl ether, ethyl vinyl ether, dimethylallyl ammonium chloride, dimethylaminoethyl acrylate, N-vinyl urea, acryloyl urea, N,N-diethylaminoethyl acrylate, N-methyl acrylamide, tert-butylaminoethyl acrylate, dimethylaminopropyl methacrylamide, methacrylamidopropyl trimethyl ammonium chloride, and hydroxyalkyl esters of ethylenically-unsaturated monocarboxylic acids having from 3 to about 22 carbon atoms, such as hydroxyethyl acrylate. Termonomers which are presently preferred comprise (meth)acrylic acids and their monovalent salts and their esters such as methyl acrylate, butyl acrylate, methyl methacrylate and lauryl methacrylate, acrylonitrile, diacetone acrylamide and styrene for increasing the hydrophobic character of the terpolymers, vinyl pyridines, hydroxypropyl methacrylate and hydroxyethyl methacrylate and hydroxyethyl acrylate as water soluble monomers which increase the hydrophilic character of the terpolymers without introducing termonomers which are sensitive to metal cations (and because good results have been obtained with 4-vinylpyridine and 3-methyl-2-vinylpyridine); and vinyl acetate due to its low cost and ready availability.

As with the copolymers, the monomer weight ratios of the terpolymers can vary rather widely, depending upon the intended application, but preferably the termonomer will be present as no more than about 10 weight percent of the monomer units charged. More broadly, however, particularly with non-ionic hydrophilic termonomers up to 25 weight per cent can be used. The first and second monomer units can be present in approximately the range of weight ratios disclosed for the copolymers, constituting the major portion of the terpolymer, with the termonomer providing the remaining minor portion. For example, the terpolymer can consist of 45 weight percent each of the first and second monomers, with 10 weight percent of the termonomer, 49 weight percent each of the first and second monomers with 2 weight percent of the termonomer, and so on. These examples contain the first and second monomer

units in weight ratios of 50:50, but as disclosed above, the three monomer units can be combined in any combination, provided the termonomer does not exceed 10 weight percent, but preferably is at least 1 weight percent, and the first and second monomer units are within the range of weight ratios as disclosed for the copolymers. Based on the examples, the termonomer is preferably present as from about 2 to about 8 weight percent, or more preferably, from about 3 to about 5 weight percent, based upon total monomers.

As the copolymerization reaction produces polymer in near-quantitative yield, the desired ratios of VP to Am can be obtained by controlling the ratios of VP monomer and Am monomer charged to the reactor and the rates at which the monomers are fed into the reactor.

Another significant aspect of this invention is described as follows. Polyacrylamide has historically been a standard material for thickening water for oil recovery. At a concentration of, for instance, 0.25 weight percent in sea water, polyacrylamide imparts a viscosity to the resulting solution which is about ten to twenty times the viscosity of sea water at the same temperature. For instance, sea water at room temperature has a viscosity of approximately 1 compared with 10 to 25 for the same water containing a quarter weight percent polyacrylamide and this viscosity remains essentially unchanged on aging at room temperature. At 250° F (121° C.) sea water has a viscosity of about 0.3. The same water with 0.25 weight percent acrylamide initially has the viscosity of about 10 but on aging the acrylamide precipitates rendering it totally useless with the resulting sea water not having a viscosity increased any after the precipitation.

The following description of FIGS. 15 and 16 show that in accordance with the invention, significant enhancement of the viscosity of polymer flood water is possible even when the water is to be used in reservoirs exhibiting hostile conditions.

In FIGS. 15 and 16 the viscosity data is for polymer aged 7 days at 300° F and then the viscosity determined at 250° F. The 300° F aging test is carried out as follows. Synthetic sea water (SSW) is prepared from distilled water to which salts are added as described hereinafter. The polymer is dissolved in the SSW to form a 0.25 weight percent solution. It is then subjected to vacuum and if necessary nitrogen purge to remove oxygen. It is then sealed under 100 psig nitrogen pressure in a glass lined container and aged 7 days at 300° F.

As can be seen from FIG. 15, polymer compositions depicted therein have aged viscosities of 0.7 (i.e. better than 2 times sea water) or greater, generally 1.0 (about 3 times sea water) or greater. Thus in accordance with this invention for the first time the psychological barrier has been crossed to utilizing polymers which do not impart the 10 to 20 fold increase in viscosity associated with standard materials such as acrylamide. The inventors have surprisingly discovered that the water soluble polymers described herein because of their resistance to precipitation on aging at high temperatures are effective in spite of their apparent poor performance in standard room temperature viscosity tests. In high temperature applications the only significant factor is the viscosity imparted after aging.

The polymers shown in area B of FIG. 15 represent compositions which are preferred because of stability even at 250° F. Those of area E are useless because of precipitation at hostile environment temperatures of

170° F Areas D and C represent polymers stable up to at least 170° F and 200° F respectively. The area encompassed by area B can be increased somewhat by utilizing N,N-disubstituted acrylamide as shown in FIG. 16. The area encompassed in region A is less preferred because the viscosity imparted to the sea water is so low that higher concentrations are required to give effective solutions. Such compositions are not useless, however, and can be used if desired with best results obtained using the highest molecular weight polymers obtainable.

As stated hereinabove the unaged viscosity at an arbitrary test temperature of 250° F (121° C.) for a solution containing 0.25 weight percent polyarylamide unaged is about 10. For polymers as shown in FIG. 15 having aged viscosities of 1 the unaged viscosity is about 1.5. Other polymers depicted as being encompassed by the useful polymers in accordance with this invention can have unaged viscosities at 250° F (121° C.) of about 2 or slightly more (some specific compositions are higher than this). Thus the invention in one aspect can be viewed as utilizing a polymer in a hostile environment which polymer in an unaged test at 250° F in a concentration of 0.25 weight percent imparts to sea water a viscosity of less than one third (i.e. a viscosity of no more than 2 or no more than 3) the viscosity imparted by the same amount of a standard unaged acrylamide polymer such as N-Hance 1027 by Hercules.

In another aspect, the invention resides in the surprising relationship wherein the N-vinylamide such as VP imparts a disproportionate stability to the polymers containing pendant amide groups such as Am derived polymers as well as copolymers of unsaturated amides such as acrylamide and vinyl-containing sulfonate monomers such as AMPS, i.e. VP/Am/NaAMPS. Yet VP does not stabilize the esters discussed hereinafter (such as SPM). In fact, the VP/SPM is not as effective as the SPM homopolymer. SPM represents, e.g., potassium or sodium 3-methacryloyloxy propanesulfonate or (3-sulfo-3-propyl) methacrylic ester, sodium or potassium salt.

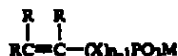
In order to distinguish between the N-vinyl lactam and unsaturated amide comonomers which are hydrophilic and non-ionic or neutral on the one hand and the sulfonate comonomer which is also hydrophilic but

anionic on the other hand, the sulfonate is arbitrarily referred to as the "third comonomer". This then further distinguishes from the monomers referred to as monomers which are generally hydrophobic or if hydrophobic are not anionic.

The third comonomer is referred to as a vinyl-containing sulfonate which is meant to encompass the acid also. They are represented by the following formula.



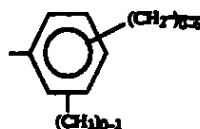
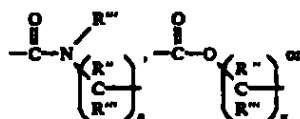
Also the analogous phosphonate compounds are represented by the following formula can be used



where in each formula R is methyl, ethyl or H preferably methyl or H and provided further that at least one of the R groups on the terminal carbon of the vinyl group is H and the other is H or methyl. In another embodiment, the non-terminal R can be a group which will make the vinyl group more reactive. As an example, R can be a nitro group.

M in each formula is H, Na⁺, K⁺, Li⁺, R^{'''}₄N⁺, Ca⁺⁺ or Mg⁺⁺ and

X in each formula is



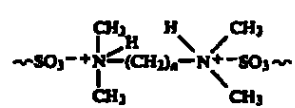
where n is an integer of 1-5 preferably 1-3 and R^{'''} is individually selected from 1-3 carbon atom alkyl groups, or H, R^{'''} is selected individually from H, -ROH or a 1-3 carbon atom alkyl radical.

In a broader embodiment, M can be selected from those cations recited above and in addition can be other polyvalent metals such as Zn⁺⁺, Sr⁺⁺, Fe⁺⁺, and Mn⁺⁺. Other cations are organic cations of the formula +NH₃R¹NH₃⁺ where R¹ is 1-20 carbon atom divalent hydrocarbon radical. Examples of organic cations are those formed from methylamine, diethylamine, ethylene diamine, tetramethyl ethylene diamine, long chain diamines such as C₁₂ diamines and N-propylammonioethanol. Polyether diamines are particularly suitable. Such materials are sold under the tradename Jeffamine ED-600, ED-900 and ED-2001 and have the following general structure



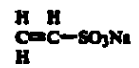
where a+b is 2-3 and n is 8-41. Another particularly desirable class of amines is the multi-basic amines such as poly(ethylenimine). The acid form of the monomer can be reacted with the polyether diamines in water or a solvent such as DMF, DMSO, alcohol or mixtures thereof and the salt precipitated and isolated. In the case of aqueous systems, the monomer generally is added last. In some instances, there may be a preference for tertiary amines instead of the primary.

In the case of polyvalent cations the resulting monomer units which are [CR₂=CR(X)_{0.1}-SO₃]₂M and a small amount of [CR₂=CR(X)_{0.1}-SO₃]₁M have a greater molecular weight and also have the potential for crosslinking in the resulting polymer. While not wishing to be bound by theory, the use of such divalent cations can be viewed as creating an ionic crosslinking of two or more monomer units, i.e.

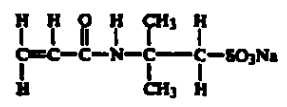


After polymerization this in effect gives crosslinking between polymer chains thus increasing the molecular weight and hence increases the viscosity the resulting polymer will impart to water. However, surprisingly the most dramatic effect is to give more stable polymer in copolymerizations with unsaturated amides such as acrylamide. While not wishing to be bound by theory, apparently the polyvalent cation monomer is more nearly equal to or greater than the acrylamide in reactivity and thus avoids long segments of polyamide homopolymer blocks from being formed which render the entire molecule unstable. This increased stability is particularly remarkable in polymer compositions having 10 weight percent or greater, i.e., 10-90, preferably 10-50 weight percent of the unsaturated amide. Indeed, the difference in hydrolysis resistance of copolymers produced from monomer salts of the various metals, primary, secondary, and tertiary or diamines allows fine tuning of the properties of the final polymer to suit a particular end use.

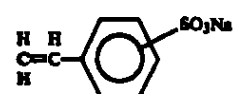
Salts of the metals and amines listed above such as chlorides, sulfates and carbonates, e.g. NaCl, CaCl₂, MgCl₂, Na₂SO₄, and especially (NH₄)₂C₂O₄ or combinations thereof can be added to the already produced polymer to improve ease of drying, to make the polymer more easily redissolved and to inhibit amide formation. Examples of suitable monomers are



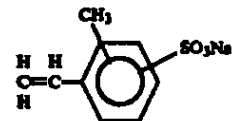
vinyl sulfonate, sodium salt



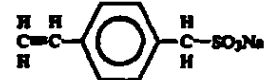
sodium-2-acrylamido-2-methylpropane sulfonate (sodium AMPS)



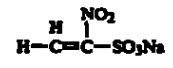
styrene sulfonate, sodium salt



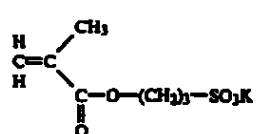
sodium vinyl toluene sulfonate



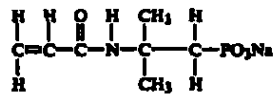
sodium p-vinylbenzyl sulfonate



-continued
1-chloroethylene sulfonic acid, sodium salt

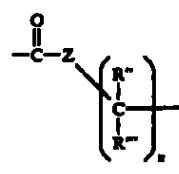


(3-sulfopropyl) methacrylic ester, potassium salt (SPM)

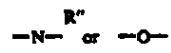


2-acrylamido-2-methylpropane phosphonic acid, sodium salt

The first two formulae for X can be viewed as



wherein Z is



i.e., amides or esters. Of course, mixtures of these amides and esters can also be used.

These are known monomers and can be produced as is known in the art. Particularly with regard to the N-sulfohydrocarbon-substituted acrylamides, they are disclosed in U.S. Pat. No. 3,679,000 assigned to the Lubrizol Corporation, the disclosure of which patent is incorporated by reference. The 2-acrylamido-2-methylpropanesulfonic acid is available from Lubrizol under the designation AMPS.

Purified AMPS monomer results in surprisingly superior polymer. While not wishing to be bound by theory, it is believed the higher purity results in higher molecular weight which is responsible for the increased viscosity imparted to water by polymer made from purified monomer. Preferably the monomer is purified to contain less than 150 ppm, preferably less than 50 ppm by weight chain transfer-promoting impurities such as allylic compounds. This is done by recrystallization from hydrous acetic acid or lower alcohols, chromatographic techniques or other standard purification procedures.

Thus useful compositions can be described as polymers produced from a monomer composition comprising at least one of a hydrophilic N-vinyl lactam (more broadly an N-vinyl amide) or a hydrophilic vinyl containing sulfonate salt or the corresponding acid, optionally containing in addition a hydrophilic unsaturated amide and if desired a termonomer as disclosed hereinabove, said polymer being stable. Not precipitating after 7 days at 300° F (149° C) is one way of defining stability which has been definitely correlated with long term stability at 250° F for N-vinyl lactam/unsaturated amide polymers. Particularly with the N-vinyl lactam containing polymers, after a modest initial drop in viscosity on aging, the viscosity on continued aging remains essentially unchanged. Because of this enhance-

ment of stability on extended aging these N-vinyl lactam containing polymers are particularly suitable for extremely harsh environments as defined for instance by the area above the 20 day line or even the 5 day line or 1 day line at FIG. 14. By N-vinyl lactam containing polymers as used in this context of extremely harsh environment stability is meant polymers having at least 20 weight percent combined N-vinyl lactam and unsaturated amide, at least half of which is N-vinyl lactam.

In certain applications it is believed there is an advantage to copolymer compositions having at least 20 weight percent each of the vinyl-containing sulfonate and the N-vinyl lactam (more broadly N-vinyl amide) and 0-40 weight percent of the unsaturated amide. In other instances compositions having at least 10 weight percent of all three monomers (lactam, amide and sulfonate) are preferred.

Polymers of 80-95, preferably 85-90 weight percent sodium AMPS and 5-20 preferably 10-15 weight percent VP are particularly suitable for water loss polymers. Such polymers are of particular utility in high temperature geothermal drilling fluids particularly those not employing the clay usually associated with drilling fluids. These polymers are also especially suited for coating weighting agents to reduce abrasion of Densimax-type iron ore.

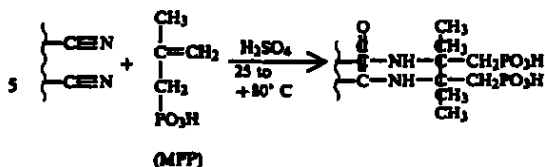
The following is a more detailed discussion of the phosphonate-containing compositions. The 2-acrylamido-2-methylpropanephosphonic acid (AMPP) or its salts (the metal being as defined for M hereinafter) can be prepared as described in German Offenlegungsschrift DE 3,210,775 (Sept. 29, 1983), the disclosure of which is hereby incorporated by reference.

For reservoirs with temperatures in the range of 170 to about 230 F the homopolymer of AMPP or its copolymers (including 3 or more monomer combinations) with acrylamide (Am), AMPS or its salts, methacrylamide, N,N-dimethylacrylamide, vinyl acetate, acrylonitrile, or 2-vinylpyrrolidone (VP) may be used. However, as the temperature increases within this range the Am content in the copolymers must be reduced.

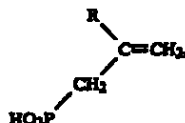
For reservoirs with higher temperatures and appreciable hardness levels, the 2-acrylamido-2-methylpropanephosphonate co- and terpolymers with VP are preferred because of their improved retention of viscosity. Thus, with phosphonate copolymers, reservoirs with temperatures of about 230F or higher require copolymers of AMPP with VP; terpolymers of AMPP, AMPS (salts, especially Na⁺), and VP; terpolymers of copolymers of AMPP, AMPS (salts), VP, and Am or DMAM.

These phosphonate-containing polymers may be prepared in the manner described hereinafter in more detail, i.e., by solution polymerization in water, in gel form, in suspension or slurry or by inverse-emulsion polymerization. Initiation may be accomplished by typical chemical agents such as azo compounds, hypodinites, paramenthane hydroperoxide + FeSO₄·7H₂O, potassium persulfate, etc. or by radiation (α-rays, electron beam, UV, etc.). The preferred method will be the one that supplies the highest molecular weight in a conveniently used physical form.

In a different aspect of this invention, phosphonic acid or a composition containing phosphonate groups can be added to a preformed polymer which contains pendant nitrile (—C≡N) units, along with H₂SO₄ or some other strong acid in water at -25° to 80° C., i.e.



The 2-methylpropenephosphonic acid (MPP) shown above can be synthesized from isobutylene, PCl₃, and SO₂ as described in said DE 3,210,775. Other phosphonated alkenes also may be used, however, for stability the carbon which is attached to the nitrogen in the functionalized polymer must be disubstituted. That is,



where

R=alkyl, phenyl, etc. R=H

Various derivatives of the phosphonic acid may also be made prior to the reaction onto the polymer, provided these derivatives are stable in the presence of strong acid.

Polymers with pendant nitrile groups consist of polyacrylonitrile and copolymers of acrylonitrile such as poly(acrylonitrile-co-styrene), poly(acrylonitrile-co-acrylamide), poly(acrylonitrile-co-N-vinyl-2-pyrrolidone-co-acrylamide), poly(acrylonitrile-co-methacrylic acid), poly(acrylonitrile-co-acrylic acid), poly(acrylonitrile-co-N-vinyl-2-pyrrolidone), poly(acrylonitrile-co-methylmethacrylate).

Polymer Characterization

The polymers of this invention can be characterized as to relative molecular weight and viscosity by K values calculated from measured relative viscosities η_{rel} at various concentrations. In this calculation, K=100 k, where k is Fikentscher's constant, obtained from the equation

$$\frac{\log \eta_{rel}}{C} = \frac{75 k^2}{1 + 1.5 kC} + k$$

where η_{rel} is the viscosity of the solution compared with its solvent and C is concentration in grams per 100 milliliters (or 1 deciliter) of solution. The development and significance of K values are discussed more fully in Example VIII.

In contrast to the copolymers of 50-99 mole percent N-vinyl-2-pyrrolidone and 1-50 mole percent acrylamide, with K values of 10 to 140, disclosed and claimed by U.S. Pat. No. 3,500,923, the copolymers of this invention have K values of more than 140 when measured at concentrations of 1 gram/deciliter or less. The highest K values generally correlate with the preferred methods of preparation and testing of the copolymers of this invention, as described in example VIII. Copolymer solutions prepared and tested by the methods presently considered optimum can have K values in the range from of about 150 to at least about 250.

The polymers of this invention can be further characterized by measuring the cloud point temperature, as defined and more fully discussed herein and in Examples V, VI and XVII. The polymers are preferably tested for cloud point temperatures at heat aging for a period of time which produces an equilibrium cloud point temperature representative of the polymer's performance in, e.g., enhanced oil recovery in reservoirs of equivalent temperatures. The equilibrium cloud points appear to correspond to an equilibrium degree of hydrolysis, as defined elsewhere herein, generally limited to about 70-80 percent, which may partially account for the superior properties of the preferred copolymers.

Polymerization

The polymers of this invention can be formed using solution, emulsion, inverse emulsion (water-in-oil) or slurry polymerization processes. In one embodiment of the invention, a process for producing the polymers comprises carrying out the polymerization in a homogeneous solution process in which the polymerization medium is water containing certain dissolved mixed electrolytes, or presently most preferably, water containing appropriate dissolved salts such as found in sea water, to provide a simulated or synthetic sea water (SSW). Natural sea water and formation brines can also be used in the polymerization media and can be filtered to remove solid material if desired or necessary. Brines containing a high percentage of dissolved solids can be diluted with fresh water to provide an appropriate concentration of dissolved solids. Alternatively, salts can be added, if deemed necessary to obtain the desired salt level. In another embodiment, slurry polymerization is preferably conducted with a polymerization medium consisting essentially of an alcohol, preferably a neat tertiary alcohol which generally has from 4 to about 8 carbon atoms, most preferably t-butyl alcohol, since the polymeric product is insoluble in the alcohol and can thus be conveniently separated.

In accordance with one embodiment of the invention, the inventive processes can be used to prepare the inventive polymers by carrying out the polymerization out in a polymerization medium using monomer concentrations ranging broadly from the minimum required to produce a polymer solution of the desired viscosity, e.g., as low as 0.1 weight percent, up to very concentrated solutions which amount to admixtures of the monomers with a minor amount of the polymerization medium, e.g., as high as 80 weight percent monomers based on the monomers plus medium. The polymers prepared in the preferred media in monomer concentrations over this broad range will all exhibit stable viscosities, when exposed to hostile environments of high temperature and/or salinity and/or hardness, but will not be as viscous as those prepared at optimum monomer concentrations. However, the polymers are generally produced from solutions of total monomer concentrations ranging from about 5 to about 50 weight percent. Preferably, polymerization is carried out in a solution of total monomer concentration in the range from about 10 to about 40 weight percent, since the use of monomer concentrations below about 10 weight percent tends to be uneconomical, and optimum polymer viscosity is generally obtained at less than about 35 weight percent monomers. Also, when a high concentration of electrolytes is to be used in an aqueous medium, the higher concentrations of monomers may inhibit the solubility of the electrolytes. For free radical initiation in aqueous

media containing electrolytes, monomer concentrations in the range of from about 15 to about 35 weight percent are most effective, with concentrations of about 20 to 30 weight percent particularly preferred. For alcoholic media, monomer concentrations in the range of from about 15 to about 35 weight percent are most effective, with concentrations of about 20 to 30 weight percent particularly preferred.

For a given polymer and set of polymerization conditions, the viscosity obtained will reach a maximum for a certain range of monomer concentrations in the polymerization medium, generally lying between about 20 to about 50 weight percent. Reaction rate increases, thus reaction time decreases, as the weight percent of monomers is increased. Thus, it is generally desirable to use a concentration of monomers which will produce a polymer of maximum viscosity in a reasonable reaction time. Other considerations are the actual viscosity required of the polymer in its applications, solubility of the polymer in its applications, solubility of the polymers in water, and transportation/handling expenses.

The SSW used for preparation of many of the polymers described herein (unless otherwise indicated), for example, was prepared with the ingredients tabulated below to contain the following quantities of dissolved salts.

Compound	Quantity
NaHCO ₃	3.69 g
Na ₂ SO ₄	77.19 g
NaCl	429.00 g
CaCl ₂ ·2H ₂ O	29.58 g
MgCl ₂ ·6H ₂ O	193.92 g
H ₂ O, distilled	to 18.0 liters mark

This "recipe" was calculated to produce the ionic concentrations tabulated below.

Ion	Concentration, ppm
Na ⁺	10,530
Ca ⁺²	437
Mg ⁺²	1,256
HCO ₃ ⁻	145
Cl ⁻	18,540
SO ₄ ⁻²	2,828
Total	33,756

This was equivalent to a total concentration of dissolved salts of about 3.4 weight percent, or an anionic strength of about 0.7. The divalent hardness cations (Ca⁺² and Mg⁺²) amounted to about 16 weight percent of the total cations. Various combinations of such salts can be used to prepare solutions with ionic concentrations approximating those of sea water from various locations.

Electrolyte-containing SSW polymerization media employed in the invention can have salinity values ranging from about 10 to 100 g per kg, and preferably from about 30 to about 43 g/kg, of the solution. Salinity is defined as the total dissolved solids in sea water. In natural sea water, salinity and chlorinity are related by the expression $\text{salinity} = 1.835 \times \text{chlorinity}$, according to "The Oceans, Their Physics, Chemistry and General Biology", by H. V. Sverdrup, M. W. Johnson and R. H. Fleming, Prentice-Hall, Inc. 1942, p. 51. Thus, calculated chlorinities corresponding to salinities of 30 to 43 g/kg of solution range from about 16 to about 23 g/kg.

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of solution. The ionic strengths of the solutions corresponding to these ranges vary from about 0.6 to about 0.9. It can readily be seen that a salinity of 100 g/kg is approximately equivalent to 10 percent dissolved solids, based upon the weight of the solution.

The Sverdrup reference, on p. 55, states that salinity in the oceans generally lies between about 33 to 37 g/kg sea water but may reach 40 g/kg sea water or more in certain locations such as the Red Sea. However, the reference states, on p. 165, that regardless of the absolute concentration of dissolved solids, the ratios between the more abundant substances remain virtually constant. Preferably, synthetic sea water compositions should have approximately this ratio, although the overall concentrations can vary.

A composition for simulated sea-salt for preparation of "substitute ocean water" (SOW) is disclosed in ASTM D-1141 (1982, part 31, p. 1074). The composition contains the following compounds which when dissolved in water at the quantities shown to make a liter of solution will provide a substitute ocean water for testing purposes. The materials and the quantities required to make a liter of solution are shown in the table

TABLE 1

Substitute Ocean Water, ASTM D 1141		
Compound	g/L	Weight Percent
NaCl	24.53	68.08
MgCl ₂	5.20	14.43
Na ₂ SO ₄	4.09	11.35
CaCl ₂	1.16	3.22
KCl	4.695	1.93
NaHCO ₃	0.301	0.56
KBr	0.101	0.28
H ₃ BO ₃	0.027	0.07
SrCl ₂	0.023	0.07
NaF	0.003	0.008
Totals	36.032	99.998
Ba(NO ₃) ₂	0.0000994	
Mn(NO ₃) ₂	0.0000340	
Ca(NO ₃) ₂	0.0000308	
Zn(NO ₃) ₂	0.0000096	
Pb(NO ₃) ₂	0.0000066	
AgNO ₃	0.0000049	

The compounds above the line generally comprise those used in making substitute ocean water. Such a product is commercially available as "sea salt" from Lake Products Co., Inc., Ballwin, Mo. Substitute ocean water at a concentration of about 4.1 weight percent was used in Example XXII. The trace amounts of the compounds listed below the line can be optionally included to more closely approximate ocean water when desired.

The chlorinity of the 10 component system (Table 1) used in preparing the substitute ocean water is about 19.26 g/kg solution, counting the bromide and fluoride ions as chloride ions. This corresponds to a calculated salinity of about 35.3 g/kg solution. The total dissolved solids are 36.03 g/L of solution, which amount to about 3.5 weight percent of the solution.

At a constant weight ratio of components as indicated in Table 1, the weights of each component can be calculated at various salinities for the 10 component system. The calculated weights, total dissolved solids and estimated weight percent thereof based on 1 liter of solution and the calculated ionic strengths thereof are given in Table 2.

TABLE 2

Calculated Component Ranges for Substitute Ocean Water Salinities				
Component	30	33	40	43
NaCl, g	20.85	22.93	27.80	29.88
MgCl ₂ , g	4.42	4.86	5.89	6.33
Na ₂ SO ₄ , g	3.47	3.82	4.63	4.98
CaCl ₂ , g	0.986	1.08	1.31	1.41
KCl, g	0.591	0.650	0.788	0.847
NaHCO ₃ , g	0.171	0.188	0.228	0.245
KBr, g	0.086	0.094	0.114	0.123
H ₃ BO ₃ , g	0.023	0.025	0.031	0.033
SrCl ₂ , g	0.021	0.023	0.028	0.030
NaF, g	0.0025	0.0028	0.0034	0.0037
Total Dissolved Solids, g	30.62	33.67	40.88	44.28
Wt. % Solids	3.0	3.3	4.0	4.3
Calculated Ionic Strength	0.60	0.67	0.81	0.87

The data presented in Table 2 show that the calculated ionic strengths for salinities varying from 30 g to 43 g per liter of solution range from about 0.6 to about 0.9.

At a constant weight ratio of the 5 component SSW system generally used in the invention, the weights of each component are calculated for salinities ranging from 30 g to 43 g per liter of solution. The calculated weights, total dissolved solids and estimated weight percent thereof based on 1 liter of solution and the calculated ionic strengths thereof are given in Table 3.

TABLE 3

Calculated Component Ranges For Synthetic Sea Water (SSW) Salinities				
Component	30	35.3 (SSW)	38	43
NaCl, g	19.950	23.830	25.650	29.030
MgCl ₂ , g	4.288	5.046	5.432	6.147
Na ₂ SO ₄ , g	3.644	4.288	4.616	5.223
CaCl ₂ , g	1.396	1.643	1.769	2.001
NaHCO ₃ , g	0.174	0.205	0.221	0.250
Total Dissolved Solids, g	29.452	35.012	37.688	42.631
Wt. % Solids	2.9	3.4	3.7	4.1
Calculated Ionic Strength	0.59	0.70	0.76	0.86

The presently preferred polymerization medium used to produce the polymers of this invention is the 5 component system shown in Table 3 above having a calculated ionic strength of about 0.7 and about 3.4 weight percent dissolved solids. It is expected that polymerization media shown in the various tables, regardless of the number of components present in the media, which have calculated ionic strengths ranging from about 0.6 to about 0.9, will also be highly suitable in preparing the various outstanding polymers of this invention. Also, more concentrated or more dilute versions of these SSW compositions, having ionic strengths in the range from about 3.0 to 0.2, can be prepared and used as polymerization media for this invention.

On the other hand, the aqueous polymerization media of this invention can be based on oil field brines, at natural or dilute strength. Such brines can be filtered or otherwise purified to remove undesirable solid matter.

Oil field brines can contain up to about 25% by weight, based on water, of dissolved inorganic salts. In addition to NaCl, brines usually contain up to about 10% by weight, based on the total amount of salts present, of Ca⁺² and Mg⁺². Small amounts of other soluble

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Periodic Group I and Group II salts are also frequently present, e.g., NaHCO_3 , KCl , BaCl_2 and the like. Typical brines contain from about 1 to 14 wt %, based on water, of dissolved salts.

Although the reasons for the superiority of aqueous polymerization media containing electrolytes are not presently understood, polymers prepared in such media have been found to have higher viscosities and higher K values than similar polymers prepared in conventional media such as distilled water. Also, these polymers are more resistant to high temperature, salinity and hardness ions, retaining their viscosity longer under such conditions than the polymers prepared using media such as distilled water, even under the imposition of high shear, as seen by the screen tests of Example IX.

A presently preferred electrolyte mixture for the aqueous polymerization media of this invention contains at least one electrolyte selected from a first group consisting of alkali metal salts and, at least one electrolyte selected from a second group consisting of alkaline earth metal salts, as an approximation to a synthetic sea water. Although not presently understood, it appears that the combination of monovalent and divalent cations is at least one property of synthetic sea water which enhances the properties of copolymers prepared in such media. Thus, it is believed that a fraction of divalent hardness cations to total cations of at least about 1 weight percent will improve a polymerization medium containing NaCl or other alkali metal electrolytes. Since the synthetic sea water used successfully contained about 16 weight percent hardness cations (based upon total cations), the polymerization media of this invention should preferably contain such a fraction of at least about 10 weight percent hardness cations, but can contain up to about 50 weight percent or even more, as with simple mixtures of the alkali metal and alkaline earth salts. The presence of certain anions may also enhance the effect of the polymerization media described herein, perhaps through a buffering action. Various concentrations of the salts can be used, generally ranging from about 0.1 to about 10 weight percent or more, preferably at least 1 weight percent, based upon the total weight of the polymerization medium. For polymers to be used in certain applications, such as, e.g., minerals recovery or beneficiation, salt concentrations of up to saturation can be advantageously used.

In addition to the use of a specified concentration of a mixture of electrolytes containing both alkali and alkaline earth metal salts, the aqueous polymerization media containing such electrolytes can be characterized by the resulting Ionic Strength, given by the formula

$$I.S. = \frac{1}{2} \sum C_i Z_i^2 = \frac{1}{2} \sum C_j Z_j^2 + \dots$$

where C_1 , C_2 , etc. each represent the molar concentration of a different ion in the polymerization media, Z_1 , Z_2 , etc. are the charges of the respective ions, both positive and negative, and n equals the number of different ions in the polymerization medium.

For further discussion of Ionic Strength, see, e.g., Fritz and Schenk, "Quantitative Analytical Chemistry", Second Edition (Allyn & Bacon, Boston, 1969), pages 9-10.

Generally, aqueous polymerization media with electrolyte Ionic Strengths in the range of from about 0.4 to about 3.0 are effective in improving the properties of the polymers of this invention, preferably, amounts of mixed electrolytes sufficient to produce an Ionic Strength of in the range from about 0.5 to about 2.0 are

used, as Ionic Strengths in this range have been found to produce significant improvements in the polymers prepared in such polymerization media. Aqueous polymerization media having Ionic Strengths of in the range from about 0.6 to about 0.8 are presently preferred for most applications, as polymers having viscosities higher than otherwise obtainable and excellent heat stability can be prepared therein. These ionic strengths "bracket" the Ionic Strength of natural sea water, which for, e.g., the North Sea, is about 0.7.

The pH of the aqueous polymerization media employed in this invention should be controlled during the polymerization process, as excessive acidity of alkalinity can adversely affect the polymerization process or result in excessive hydrolysis of the product polymer, copolymer or terpolymer. Generally a pH in the range of from 4 to about 10 is acceptable, with a range of from about 6 to about 8 preferred. An added benefit of the use of electrolytes in the polymerization media of this invention is that the combinations of electrolytes used generally will buffer the pH to a value within the preferred range, as with natural sea water.

It has been found that with copolymerization of N-vinyl lactams and unsaturated amides superior results are obtained by carrying out the polymerization at a pH within the range of 5 to 10.5, preferably 8.5 to 10.5. With vinyl containing sulfonate (or the corresponding acid) monomer systems the pH should be from 7 to 10.5 except where the "M" of the sulfonate is $\text{R}^+ \text{N}^+$, i.e. HN_4^+ , in which case the pH can be as low as 4.5. Thus in all instances a pH of 7 to 10.5 is satisfactory. In those systems not having a significant amount of the vinyl containing sulfonate the pH can be as low as 4 although generally it will be at least 5. Within this range, the resulting polymer imparts greater viscosity to water. As described in greater detail elsewhere herein, the polymerization is carried out in aqueous media preferably containing monovalent electrolytes and initiated by radiation or chemical initiators or both.

If the polymer is to be made on or near an offshore oil recovery site natural sea water would predictably be the preferred polymerization medium, due to its suitable properties and ready availability at low cost. Sea water may require treatment to render it suitable for use as a polymerization medium and/or oil recovery flooding fluid, such as, for example, filtering to remove extraneous solids such as sand and microorganisms and treatment with a biocide to prevent the growth of microorganisms. Flooding fluids should preferably be similar to and/or compatible with the formation water, as is known to those skilled in the art.

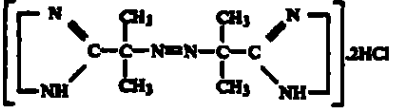
Polymerization Initiators

The polymers of this invention can be prepared by processes using various free radical polymerization initiators known to those skilled in the art. Preferred initiators include chemical polymerization initiators, the introduction of electromagnetic or nuclear radiation to generate free radicals, and combinations of both techniques.

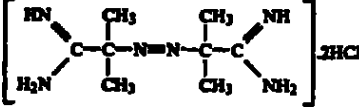
Chemical polymerization initiators employable in the polymerization processes are oil or water soluble compounds known in the art to generate free radicals for this purpose selected from azo compounds and organic peroxides such as 2,2'-azobisisobutyronitrile (commercially available as Vazo-64® from E. I. Du Pont), 2,2'-butylazo-2-cyanopropane, 2,2'-azobis(2,4-dimethyl-

valeronitrile) (Vazo-052 (R) from E. I. Du Pont), 2, 2'-azobis(2-amidinopropane) hydrochloride (V-50 from wako) 2-t-butylazo-2-cyanopropane, 2-t-butylazo-2-cyanobutane, 2-t-butylazo-1-cyanocyclohexane, benzoyl peroxide, di-t-butyl peroxide, t-butyl peroxyacetate, t-butyl peroxyvalerate, 2-t-butylazo-2-cyano-4-methoxy-4-methylpentane (commercially available as Luazo (R) 55 from Lucidol Div., Pennwalt Corp.), and hyponitrites such as t-butyl hyponitrite and t-amyl hyponitrite 2-t-butylazo-2-cyano-4-methylpentane (Luazo (R) 70, available from same source), 4,4'-azobis(4-cyanovaleric acid), 4-t-butylazo-4-cyanovaleric acid and the like. The azo compounds are presently preferred for most applications, as some peroxides appear to have a tendency to adversely affect the polymer; however, some peroxides are effective at lower temperatures than those at which most azo compounds are useful. A particularly suitable lower temperature initiator is 2,2'-azobis(2,4-dimethyl-4-methoxy-valeronitrile) commercially available as Vazo 33 from E. I. Du Pont. Presently preferred compounds include t-butyl peroxyvalerate (t-BPP) (particularly for the polymerization media of t-alkanols), Luazo 55, Luazo 70, p-menthane hydroperoxide activated by FeSO₄·7H₂O complexed with ethylene diamine tetracetic acid and reduced with sodium formaldehyde sulfoxylate (this initiator is sometimes referred to as p-menthane hydroperoxide activated with SBR, SBR being defined as FeSO₄, questax, and sodium formaldehyde sulfonate), and especially azo-bis-isobutyronitrile (AIBN), since polymers prepared in its presence generally yield more viscous solutions, e.g., higher molecular weight polymer, than those prepared in the presence of t-butyl peroxyvalerate. Luazo 70 has been found to give excellent results because, as a liquid, it is more uniformly dispersible in aquo than solids such as AIBN. Luazo 55, also a liquid, should display a similar advantage. The 4-cyanovaleric acid compounds are preferred because they are water soluble. An inert atmosphere substantially free of free oxygen or other known inhibiting materials should be provided when chemical polymerization initiators are used. Mixed initiator systems of any of the preferred initiators and a peroxide such as potassium persulfate which can be activated at low temperatures by reducing agents can be used. In this regard, the preferred initiators are Vazo 33 and the para-menthane hydroperoxide referred to hereinabove. Other preferred initiators are water-soluble azo compounds containing amidine moieties such as

V-56 2,2'-Azobis(N,N'-dimethylazanesobutyramidine)dihydrochloride



V-50 2,2'-Azobis(2-amidinopropane)dihydrochloride



which are commercially available from Wako Pure Chemical Industries. Another preferred group of initiators are the alkylhyponitrites commercially available from Catalyst Resources, Incorporated. Alkylhyponi-

trites are low temperature thermal and photochemical sources of alkoxy radicals. The parent compound is actually a trans-alkylhyponitrite with the following structural formula



wherein R^e is a C₃ to C₁₂ carbon atom hydrocarbyl radical

Chemical polymerization initiators which are substantially soluble in the polymerization media of this invention can be added directly to the monomer solution, or dissolved or dispersed in a small amount of solvent which is miscible or soluble therein before being added to said monomer solution.

Chemical polymerization initiators which are insufficiently soluble in the polymerization media of this invention in the concentration required for initiation can be added in the commercially available state or dispersed as a fine powder, but are generally more effectively employed if dissolved in a liquid soluble or miscible in the medium. For example, a water-miscible solvent such as acetone or an alcohol can be used to solubilize azobisisobutyronitrile, the preferred chemical initiator, and to disperse it in the aqueous polymerization media or alternatively it can be dissolved in the vinyl lactam monomer.

The polymers of this invention can also be prepared in processes where initiation can be achieved at least partially by irradiation by electromagnetic or nuclear radiation, e.g., gamma radiation, as known to those skilled in the art. The resulting polymers when diluted with water or SSW to a common solids level, for example 2 weight percent or less, are generally found to exhibit solution viscosities comparable to or greater than similar polymers prepared by chemical initiation. Such irradiation can be used to initiate polymerization either alone or in conjunction with the chemical initiators already mentioned as well as other commonly used free radical initiators and sensitizers. In contrast to the inert atmosphere required when chemical initiators are used, free oxygen can be present when radiation alone is used to initiate polymerization, although superior results are obtained when oxygen is excluded. While gamma radiation from sources such as Cobalt 60, Cesium 137 and Iridium 192 is presently preferred, other sources of radiation can be used, including X-rays, beams of neutrons, electrons or other charged particles, or ultraviolet light from sunlight or artificial sources. An amount and intensity of such radiation should be used effective to provide the desired viscosity and an essentially complete polymerization.

In general, ionic strength of the polymerization medium, i.e. the presence of salts enhances the viscosity of the resulting polymer with chemical initiation. The use of an ionic (salt) medium, a low level of chemical initiator in conjunction with gamma ray irradiation can be used to give a high molecular weight, linear polymer with a low degree of crosslinking. Any sequence can be used but preferably the reaction medium containing the chemical initiator is first irradiated and thereafter the polymerization is completed by the chemical means.

The intensity of the radiation, thus the dosage rate, can be varied during the process. Dose and dose rate are interdependent variables, and should be selected in tandem, and in conjunction with other relevant variables as known to those skilled in the art.

Radiation methods can be used to initiate polymerization in various aqueous and organic media. The invention polymers can be prepared by radiation polymerization in aqueous media containing mixed electrolytes, as previously disclosed, or in media consisting essentially of at least one alcohol, preferably a heat tertiary alcohol, as previously disclosed.

It has been discovered that polymers of exceptional viscosity and resistance to the adverse effects of hostile environments, e.g., high temperature, salinity, hardness ion content or alkalinity, can be prepared by a method comprising polymerizing a monomer mixture comprising N-vinyl pyrrolidone and acrylamide by free radical initiation at least partially carried out by the introduction of electromagnetic or nuclear radiation, preferably gamma radiation. Preferably an aqueous polymerization medium is used, with media comprising a synthetic sea water or mixed electrolytes as previously disclosed particularly preferred.

Radiation polymerization can be carried out over a broad range of polymerization temperatures (taken as the average temperature of the monomer solution), ranging from just above freezing to just below the boiling point of the monomer solution. However, as shown in Example XXIII, chilling the monomer solution to counteract the heating effect of the polymerization reaction can produce advantages such as higher molecular weight. Thus, in one embodiment, it is preferred to chill the monomer mixture to a temperature above freezing before, during, and/or after irradiation.

Such cooling can be facilitated by carrying out the polymerization in plastic bags or other containers with center holes and submerging the containers in a cooling bath.

Normally, about 0.05 to about 2.0 weight percent of chemical initiator based on total monomer weight is used for chemical initiation alone, with a reaction temperature in the range of about 20° to about 80° C., preferably about 50° C.

In many instances there has been found a preference for lower temperature initiation, i.e. -10° to 60° C., preferably -10° C. to 30° C., more preferably 5° C. to 25° C. At these lower temperatures a higher viscosity polymer is obtained. These lower temperatures are suitable for both chemically initiated polymer and irradiation initiated polymer, or combinations thereof. The low temperature initiation particularly lends itself to "on site" polymerization at room or ambient temperature which can even be done without any temperature control. This is of particular value where gel logs of only 20-30 weight per cent solids are prepared since transportation costs are reduced. The polymerization temperature is selected based on the decomposition behavior of the initiator and the polymerization characteristics of the monomer used. Surprisingly, in spite of the limited solubility of the low temperature initiator 2,2'-azobis (2,4-dimethyl-4-methoxyvaleronitrile) excellent results are obtained in aqueous media.

The reaction is generally substantially complete, e.g. providing substantially quantitative monomer conversion, after about 1 to about 10 hours. Smaller quantities of initiator require longer polymerization time, but produce higher molecular weights. A reaction time of about 2 hours is normally employed in bench scale processes. The resulting polymers are not necessarily isolated. Instead, the solutions are further diluted as formed to obtain the desired concentration of polymer. However, the polymers generally can be isolated, dried

and redissolved or dispersed at or near the location where they are to be used, thus minimizing transportation costs. Generally, the polymers formed in an alcoholic medium are more readily isolated, if desired, than those formed in aqueous media.

Monomer Proportions

The first and second monomer proportions for copolymers of this invention can vary widely, as previously disclosed. Generally, VP:Am weight ratios of about 10:90 to about 90:10, as applied to the mixture of monomers polymerized, are used, but copolymers having VP:Am weight ratios as low as 5:95 and as high as 99:1 can be prepared and employed for specialized applications. As used in this paragraph the term VP is meant to be generic to N-vinyl lactams and N-vinyl amides as broadly disclosed and Am is generic to unsaturated amides as broadly disclosed herein (i.e., to set out the weight ratios broadly for first monomer:second monomer) and the ratios are intended to cover "mixed" copolymers, i.e. N-vinyl pyrrolidone/acrylamide/N,N-dimethylacrylamide. Generally, the minimum amount of the VP monomer required to produce copolymers of the desired characteristics will be used. The polymers of vinyl-containing sulfonate salts, phosphonate salts (or the corresponding acids) or esters as the third comonomer or vinyl lactams (more broadly N-vinyl amides) as the first component and unsaturated amides, if present, as the second component can have monomer ratios as shown in FIGS. 15 and 16 excluding area E, although of course, proportions shown are most preferred for the specific monomers set out.

Thus, the first component (the N-vinyl amide) can be present in an amount within the range of 0-100, preferably 10-90, more preferably 30-70 weight percent based on the weight of all monomers incorporated into the polymer. The second component (the unsaturated amide) in an amount within the range of 0-80 (up to 85 in VP/Am) preferably 10-55 weight percent and the third component (the sulfonate, phosphonate or ester) in an amount within the range of 0-100, preferably 10-95, more preferably 40-90 weight percent. In all instances, there can be a termonomer present in the amount set out elsewhere herein based on the total weight of the other components, the ratios just set out hereinabove thus being the relative proportions of the first, second, and/or third components to each other.

A 90/10 NaAMPS/VP is particularly suitable for water loss control in drilling fluids. Drilling fluids in which all the hostile environment-resistant polymers described herein can be used are well known in the art. Generally, they contain finely divided clays such as bentonites, kaolin (kaolinite) or illites and also organo-colloids such as carboxymethyl cellulose or sodium polysacrylate. Frequently, quebracho and/or a sulfonated asphalt is a constituent. The polymers described herein can be present in such fluids in an amount within the range of 0.5 to 10, preferably 1 to 5 based on weight. These polymers are also capable of performing in high temperature geothermal drilling fluids, which generally have no clay, where other polymers under the same circumstances break down. The high temperature can be defined as a hostile environment defined as a temperature and divalent ion concentration above the infinite days line of FIG. 14, or more broadly, in some instance, a temperature above 170° F or more preferably above 200° F.

In addition any of the polymers having a ratio of monomers as shown can also have a termonomer present in an amount up to 25 weight per cent based on the total weight of monomers as discussed hereinbefore

For enhanced oil recovery applications, the preferred 5 copolymers of this invention comprise copolymers of N-vinyl-2-pyrrolidone (VP) and acrylamide (Am) in which the weight ratios of VP:Am preferably range from about 30:70 to about 70:30. The high proportions of VP are preferred for reservoirs having more "hostile" 10 conditions, e.g., higher temperature, salinity and hardness of the formation water. For example, copolymers for use at over 260 F should preferably contain at least about 60 weight percent VP, while copolymers for use at about 250 F can have about 50 weight percent VP 15 or more. For lower temperatures, copolymers with lower proportions of VP can be tolerated, e.g., for temperatures of about 220 to about 250 F, about 40 weight VP or more should suffice, while for temperatures as low as 200 F, the copolymers can obtain at least about 30 weight percent VP. Copolymers having VP:Am monomer weight ratios in the range of from about 65 35 to about 55:45, or about 60:40, are particularly preferred for use in high temperature EOR as these copolymers will produce the highest viscosity relative to sea water after a short equilibration time in the high temperature reservoir. For applications requiring shorter stability times, greater viscosity can be obtained from copolymers of higher acrylamide content, although these are less stable than the 60:40 compositions. While 60:40 (VP:Am) copolymers are presently preferred for long-term high temperature applications, 50:50 weight percent copolymers have displayed exceptional thermal stability in aging studies conducted in water, and particularly in SSW, at temperatures ranging from about 200 35 to about 300 F. See Examples I and II. For example, such 50:40 copolymers, employed as 2 weight percent solutions in SSW, have given clear solutions after aging at 250 F for more than 918 days (487 plus 431) while the solution viscosities remain about the same or somewhat 40 higher than when first tested. Although the majority of testing has involved the 50:50 copolymers, which are presently preferred for use at temperatures of about 240-260 F, tests of aged 60:40 (VP:Am) copolymers show that they are generally superior at temperatures above about 250 F. Additional tests of the 50:50 copolymers conducted at 300 F in SSW have shown that the solutions may turn cloudy without loss of most viscosity after a few days aging, but that the cloudiness disappears upon slight cooling. The cloudiness typically first appears at a temperature between about 260 and about 280 F. Based on these observations, it appears that a preferred upper temperature limit for long-term thermal stability for the preferred inventive 50:50 copolymers is in the range of about 280-300 F. Cloud points for the 60:40 copolymers are in the range of 290-320 F, suggesting 320 F as the upper preferred use temperature for these compositions. For certain applications, e.g., drilling fluids, some of the preferred aged or unaged polymers can be subjected to temperatures as high as at least about 330 F for periods of a few days, or temperatures as high as at least about 400 F for periods of a few hours.

While preaged copolymers of approximately 60:40 VP:Am weight ratios are presently preferred for use in high temperature enhanced oil recovery, the copolymers of this invention can be "designed" and prepared in proportions which result in properties which are optimal for various other applications. Copolymers

useful in drilling wells, including use as additives for drilling, workover and completion fluids, can have any desired weight ratios, but generally such weight ratios will be from about 30 to about 60 weight percent VP with the balance Am. The exact proportions can be chosen to produce properties comprising high viscosity and resistance to high temperatures, salinity and hardness ions which are optimal for the environment in which the drilling, workover or completion fluid is to be used. As mentioned earlier, the requirements for drilling, workover and completion fluids differ significantly, e.g., drilling fluids are normally thickened with clay, while workover fluids are preferably clay free.

In general, when conditions are less severe, e.g., the fluids are to be exposed to high temperatures, salinity and/or hardness ion concentrations for shorter periods of time, a lower proportion of VP can be used in the copolymer, thus reducing costs and increasing the viscosity attainable per unit of copolymer.

Conversely, for very hostile environments and extended exposures, as in, e.g., the polymer flooding of a North Sea reservoir, a higher proportion of VP will generally be required for effectiveness, regardless of the relative cost.

For applications requiring mainly a flocculant, as, e.g., water treatment and/or thickening, clarification of beverages, or minerals beneficiation, lower proportions of VP can be used, e.g., in the range of from about 20 to 50 weight percent, with the remainder Am. In example XXIII, a copolymer having 30% VP and 70% Am was successfully used to flocculate and remove clay from a turbid river water sample.

The terpolymers of this invention can also be tailored for certain applications by adjusting the proportions and types of monomers charged. For simplicity, the term "termonomer" is used herein to mean a monomer or monomers other than the principal monomers of N-vinyl lactam and unsaturated amide, although it is recognized that technically N-vinyl lactam and unsaturated amide are also termonomers. A minor portion of a termonomer, for example a hydrophobic compound, is included to alter characteristics of the polymer such as its tendency to adsorb on or absorb in a rock formation (Adsorption refers to the attachment of polymer molecules to the rock surface by physical or chemical means, while absorption refers to such larger scale phenomena as imbibing of the polymer solution within the pore structure of the formation rock.) Other polymer characteristics which can be altered by incorporating such a termonomer in the polymer include solubility in water, brine and oils, as well as crosslinking ability. The terpolymers of this invention have been found to be as stable as the copolymers under conditions of high temperature and/or salinity and/or hardness, as shown in Examples XV through XXI, and thus provide stable polymers with various useful properties.

The termonomer can be added in a quantity in the range of from about 0.1 to not more than about 25 weight per cent, generally not more than 10 weight percent of the total monomers charged. The major portion of the terpolymer consists essentially of the first monomer and second monomer as disclosed for the copolymers, with their relative proportions or weight ratios variable over the same range as in the copolymers to adapt the polymers for various applications.

Generally, the terpolymers can contain in the range of from about 10 to about 90 weight percent of an N-vinyl lactam or more broadly N-vinyl amide such as

N-vinyl-2-pyrrolidone as a first monomer, with a second monomer of an unsaturated amide such as acrylamide in the range of from about 90 to about 10 weight percent and the termonomer as disclosed above present as an amount in the range of from about 0.1 to about 10 weight percent, preferably from about 1.0 to about 10 weight percent. Preferably, the terpolymers contain about 25 to about 75 weight percent N-vinyl lactam, about 75 to about 25 weight percent unsaturated amide, and about 2 to 8 weight percent termonomer. A termonomer content of about 3 to about 5 weight percent is presently most preferred. For enhanced oil recovery applications at reservoir temperatures of above about 250 F, it is presently preferred that the proportions of said first monomer and said second monomer be approximately or nearly equal, i.e., that the weight ratio of the first and second monomers be in the range of about 45:55 to about 65:35.

In addition to varying the monomer proportions, the molecular weight of all the inventive polymers can be varied according to the amount of initiator used or by initiation by gamma irradiation, for example. Thus, a relatively high molecular weight may be suitable for EOR, or for flocculating suspended solids, while for drilling fluids, a lower molecular weight can be used to limit the degree of flocculation of suspended clay.

The various processes of the invention for the recovery or processing of natural resources can be improved by the use of the novel polymers prepared by the methods of this invention, as disclosed earlier, although the polymers of the prior art prepared from the same monomers can be employed as well. The advantages of employing the polymers of this invention become more apparent when the polymer is exposed to a temperature of at least about 150 F or higher. Generally, in carrying out the various processes for recovery of natural resources according to this invention the polymer is generally at least partially dissolved in an aqueous fluid, and can be introduced into subterranean formations with a fluid comprising at least one component selected from the group consisting of bases, polymeric viscosifiers, crosslinking agents, surfactants and cosurfactants, and combinations of any two or more of said components. The polymers can also be used in conjunction with carbon dioxide in carbonated waterflooding. In the various processes, said polymer can be cross-linked with various crosslinking agents. The aqueous fluid to which the polymer is exposed can have a significant salinity and/or hardness, e.g. a salinity of at least about 10 grams per kilogram of solution with a fraction of divalent hardness cations to total cations of at least about 1 weight percent, or particularly, a fraction of divalent hardness ions of at least about 5 weight percent. The polymer can be exposed to various aqueous fluids in the preparation of the polymer and polymer solutions for use in the process, in the introduction into the well bore and/or formation, or in contact with subterranean formation water. The polymers which can be used in the various processes for the recovery of natural resources include copolymers produced from monomer mixtures of N-vinyl lactams and unsaturated amides and terpolymers prepared by incorporating a minor amount of at least one termonomer, generally amounting to about 10 weight percent or less based on total weight of monomers, into the monomer mixture. The proportions of the monomers in the monomer mixture can vary over a broad range, as disclosed for the polymers produced by the methods of this invention. The termonomers can be

selected as indicated elsewhere herein for the inventive terpolymers. The polymers used in these processes and compositions of the invention will hydrolyze, and when heated in solution to a temperature such as at least about 150 F for a suitable period of time, will reach an equilibrium degree of hydrolysis and an equilibrium cloud point temperature. Generally, an equilibrium degree of hydrolysis for a given temperature (thus indicating long term stability at that temperature) will be obtained by heating at a higher temperature for a short time. For instance, heating at 300 F for 7 days gives the equilibrium degree of hydrolysis for 250 F. Heating at about 250 F for at least about 7 days gives the equilibrium degree of hydrolysis and equilibrium cloud point temperature for about 180 F. Hydrolysis of the polymers to the desired degree can also be obtained by contacting them with a base or acid, optionally while heating, as explained more fully below.

The polymer can be at least partially dissolved in a liquid which is circulated in a well bore used in certain processes of the invention, such as for example when said polymer is used as a drilling fluid, a workover fluid, or a completion fluid.

It has been discovered that the various polymers prepared in accordance with this invention, as well as some of the corresponding polymers of the prior art, can be useful in various processes such as for instance for recovery or processing of natural resources, comprising enhanced oil recovery, the drilling, workover and completion of wells for the recovery of natural resources such as oil, gas and geothermal wells, the thickening and/or treatment of water for use, and minerals beneficiation. For example, in accordance with one embodiment of the invention a process for the enhanced recovery of oil from at least one high temperature production well comprises injecting an aqueous fluid thickened with a VP/Am polymer into at least one injection well to improve the recovery of oil from the production well. In such novel applications, the VP/Am polymers can be used in conjunction with various other materials, such as bases, surfactants, cosurfactants, polymeric viscosifiers, crosslinking agents and the like, used singly or in combination.

For example, the bases can be water-soluble bases selected from the group consisting of alkali and alkaline earth metal hydroxides, ammonium hydroxide, alkali metal carbonates and chemical buffer salts which dissolve with hydrolysis to yield alkaline fluids, such as sodium phosphate, sodium borates and sodium silicates, or combinations of at least two of said bases.

Surfactants can be selected from anionic, cationic or nonionic surfactants, suitable anionic surfactants include petroleum sulfonates, alkali metal carboxylates such as sodium oleate, carboxyalkylated or sulfated polyethoxylated alkyl phenols, carboxylated or sulfonated polyethoxylated alkyl phenols, carboxylated, sulfated or sulfonated polyethoxylated alcohols or carboxylic acids, and carboxylated, sulfated or sulfonated polyethoxylated thiols. Suitable cationic surfactants include long chain fatty amines and quaternary ammonium salts of fatty amines. Suitable nonionic surfactants include polyalkoxylated compounds prepared from substrates of long chain alcohols, alkyl phenols, carboxylic acids, amines and thiols. These surfactants can be used in combinations or mixtures.

Suitable cosurfactants can be polar organic compounds selected from the group consisting of saturated and unsaturated alcohols having from 3 to about 10

carbon atoms, phenols, amines, esters, mercaptans, aldehydes, ketones, amides, sulfoxides, organic nitro compounds, organic nitriles, sulfones, urea, and polyethoxylated alcohols. These cosurfactants can be used in combinations or mixtures.

The polymers, copolymers and terpolymers discussed herein are of applicability in the mobility buffer following a micellar or microemulsion slug of the type disclosed in Hedges et al U S Pat No. 4,265,308 (May 5, 1981) the disclosure of which is hereby incorporated by reference. In this embodiment a microemulsion slug is formed in a hostile environment followed by a mobility buffer comprising water and 0.05 to 1 preferably 0.1-0.25 wt percent polymer, followed by drive water. For instance a surfactant system, generally comprising a petroleum sulfonate surfactant and a C₃-C₆, preferably C₄-C₅ alcohol cosurfactant, is injected into a reservoir to form a microemulsion in situ. Thereafter the mobility buffer is injected followed by injection of a conventional drive fluid comprising water, generally saline water. Oil is recovered at a production well spaced apart from the injection well as the drive fluid pushes the mobility buffer slug which pushes the microemulsion which sweeps the oil out of the pores in the formation and to the production well. Polymeric viscosifiers can be, for example, biopolysaccharides, cellulose ethers, acrylamide-derived polymers, or mixtures thereof.

Crosslinking agents can be selected from various suitable crosslinking agents. Examples include various aldehydes and trivalent metal cations such as Al³⁺, Cr³⁺, and Fe³⁺. Also suitable are multifunctional amines such as diamines. For example, aluminum citrate can be used admixed with the polymer or in slugs alternating with polymer slugs. Soluble compounds of Cr³⁺ or Fe³⁺ can be used, or oxidizable compounds of divalent iron such as FeCl₂ can be used in conjunction with a gaseous oxidant such as air or oxygen. Phenols or phenolic materials such as lignites can be used. Formaldehyde, acetaldehyde, chromium³⁺ and aluminum³⁺ are particularly useful in unsaturated amide and/or N-vinyl lactam polymers.

The formaldehyde can be used alone or with a phenolic compound such as phenol. The specific combination of formaldehyde and phenol requires a relatively high temperature to effect gelation. By using OH substituted phenols the reactivity can be speeded up or the reaction carried out at a lower temperature. Examples of such phenolic compounds are resorcinol and catechol, conversely, a meta director such as -C≡N or chlorine can be substituted onto the phenol to slow down the reaction. Salicylic acid can also be used.

Suitable phenolic compounds include phenol, resorcinol, catechol, hydroquinones, trihydroxyphenols, o-, m-, or p-cresol, xylenols, bisphenol A, and tannins.

More specifically, with regard to aldehydes such as formaldehyde, it has been found that phenol or a phenolic compound must be used in addition to the formaldehyde to give a gel in a reasonable time at a temperature within the range of room temperature of 300F (149° C.). However, because the polymers are inherently stable, the gels, too, are surprisingly stable even in the presence of water containing high (greater than 500, generally greater than 1000-100,000 parts per million by weight) divalent metal cation concentrations. The phenol or phenolic compound may have to be used in only trace amounts to give stable gels, i.e., gels that do not set up too quickly, at higher temperatures and with particular

polymer compositions. Generally, the formaldehyde is used in an amount within the range of 0.02 weight percent to 100 weight percent, and the phenol is used in an amount within the range of 0.02 weight percent to 100 weight percent, based on 100 weight percent polymer.

That is, in the most preferred embodiment, the mole ratio of formaldehyde to phenol is about 3:1 which is about the same as 1:1 weight ratio. Most generally, the formaldehyde is present in an amount of about 1-10 weight percent based on polymer, which if the polymer is a 1 weight percent solution in water is 100-1000 ppm based on total solution. Mole ratios of 1:1 to 5:1, preferably 2:1 to 4:1, also work quite well as does the entire range described hereinabove under the proper conditions. It is noted that the crosslinking with formaldehyde utilizes amide groups in the polymer chain. At least about 4 weight percent amide comonomer is required to effect gelation.

Gelling with multivalent cations occurs when there are pendant carboxylic acid or acid salt groups in the polymer chain either from hydrolysis of acrylamide or from copolymerizing with an acid or acid salt such as acrylic acid or sodium acrylate as described in detail hereinafter.

Alternatively, a urea-formaldehyde crosslinking system can be prepared by reacting formaldehyde with urea in a mole ratio of 2-6 moles formaldehyde to one mole of urea, more preferably a mole ratio of about 4:1 is used. The reaction is carried out in aqueous medium. This mixture, with phenol, forms gels. In operation, then, a water slug, thickened with a polymer having crosslinking sites such as pendant carboxamide groups in admixture with the gelling agent is injected into a well to form a gel to effect permeability contrast correction to divert subsequent drive fluids or steam to relatively oil-rich less permeable zones. Examples of suitable polymers are NaAMPS/Am and VP/NaAMP-S/Am either partially hydrolyzed or containing acrylic acid or an acrylate as described hereinafter. Alternatively, the components can be injected sequentially (preferably the polymer is injected first) so as to effect all of the gelation in-situ.

By varying the amount of crosslinking ingredients, particularly the phenol or phenolic compound, the amount thereof and the pH (preferably at greater than 7.5) the gelation rate can be tailored to the particular reservoir. In addition to near-well treatment, these crosslinked polymers are also useful in steam flood operations, as for instance where an aqueous surfactant system and a polymeric thickener are injected with steam to give a foam to divert subsequent drive fluid. For in-situ gelation, any one of three components: polymer, phenolic compound or formaldehyde can be withheld and injected later to cause gelation.

For crosslinking with trivalent metals, some acid must be present. This can come from acid produced through preparation and/or aging because of hydrolysis or acid such as acrylic acid can be added during the preparation.

More specifically with regard to bivalent metal/oxygen gelling systems for permeability correction, in a water permeability correction process involving the in situ polyvalent metal crosslinking of polymeric viscosifiers such as polyacrylamide triggered by the sequential injection of (1) an oxidizable bivalent metal such as in a bivalent iron compound (e.g. FeCl₂) and (2) a gaseous oxidant such as air or oxygen, viscosifiers prepared by the reaction of N-vinyl-2-pyrrolidone with

one or more ethylenically unsaturated comonomers such as acrylamide, methacrylamide, vinyl acetate, acrylic acid, acrylate esters and the like are used. This system is of particular value under hostile environment conditions. This crosslinking procedure is more specifically described in U.S. Pat. No. 3,658,129, the disclosure of which is hereby incorporated by reference. That is, the presence of the carboxylic acid or more preferably the salt during polymerization gives pendant carboxylate groups from the polymer chain which form crosslinking sites.

Also, redox systems such as sodium dichromate and sodium bisulfite as disclosed in U.S. Pat. No. 3,749,172, the disclosure of which is hereby incorporated by reference can be used.

Alpha-, beta-carboxylic acid such as acrylic acid, particularly in the salt form can also be used as a fourth comonomer with the N-vinyl amide, unsaturated amide and vinyl-containing sulfonate, or simply as a comonomer with the N-vinyl amide and the unsaturated amide or vinyl-containing sulfonate, or as a comonomer with the vinyl-containing sulfonate and the unsaturated amide.

It has been found that the salt of acrylic acid imparts far greater stability to the polymer as measured by shelf life (ability to remain water-soluble on standing at room temperature or temperatures likely to be found in storage) than the acid itself. Any salt can be used including salts of divalent metal cations but generally sodium acrylate is used. Thus the result can be obtained by copolymerizing a salt of acrylic acid with the other monomers or by hydrolyzing an unsaturated amide-containing polymer under alkaline conditions, the former being preferred. In emulsion polymerization, the acid can be used quite satisfactorily.

The use of acrylic acid or an acrylate can be viewed as replacing 5-50, preferably 8-40 weight percent of one of the other monomers (generally the unsaturated amide with the acrylic acid or acrylate to provide crosslinking sites. Of particularly suitable composition is a 30/190/55/5 weight percent VP/Am/NaAMPS/-sodium acrylate polymer. That is compared with a 30/15/55 composition, the 30/10/55/5 has 33 1/3 percent of the acrylamide replaced with sodium acrylate. Broadly the acrylic acid or acid salt can be used in an amount within the range of 1-30, preferably 2-15 weight percent, the remainder including at least one of a hydrophilic N-vinyl amide or a hydrophilic vinyl containing sulfonate salt or sulfonic acid. Salts of substituted acrylic acid such as methacrylic acid can also be used as well as salts of higher unsaturated acids including those with up to 8 carbon atoms. In such cases the same conditions and concentrations set out for the acrylate also apply. In absolute terms the copolymer will contain about 1-20, preferably 2-15 weight percent of the acrylic acid or acrylate salt monomer.

The acrylate salt can also be used simply as a comonomer to provide the polymers used in this invention. It has been found that with otherwise identical monomer systems, those using the acrylic acid monomer are unsuitable because the polymers produced have a shortened shelf life; whereas, those systems using the acrylate salt monomer produce polymers possessing a much longer shelf life.

Thus, while either the acid or salt form can be used to produce gelled polymer, only the salt form has the long shelf life desired.

Any suitable amount of the polymers, including the polymers of the invention as well as analogous polymers of the prior art, can be used in the embodiments of the invention concerning the recovery and processing of natural resources. Generally, the inventive polymers prepared by the novel methods of this invention can be used in smaller quantities due to their superior properties, and are thus preferred.

For example, in the introduction of the polymers (of the invention or prior art) into a subterranean well bore a subterranean formation in processes for enhanced oil recovery, a small but effective amount of polymer should be used to produce the desired viscosity or other properties in the injection fluid. Based upon the properties of the formation and the intended nature and duration of the process, the type and amount of the polymer should be selected to achieve the desired effects over the appropriate time period. As a general guide, the amount of polymer used will be in the range of from about 500 ppm to about 10,000 ppm, preferably 1,000 ppm to about 3,000 ppm, based on the weight of the injection fluid. For gelation, 5,000 to 10,000 ppm polymer is preferred. Generally the goal will be to select an economical amount and type of polymer to produce the desired effect for the required time. Those skilled in the art can determine the amount of polymer to be used by suitable experiments carried out in light of this disclosure.

In some cases the use of polymers prepared in accordance with this invention in conjunction with such other materials can present particular advantages. For example, because of like charge interchain repulsion (including the polymer-surfactant complex) when such polymers are in an electrolyte solution with a surfactant, these systems should demonstrate increased saline resistance, and thus increased viscosity stability. The polymers of this invention can be used to improve the process of drilling a borehole in a subterranean formation, by circulating in the borehole a drilling fluid comprising the polymer, so that the high temperature water loss of the drilling fluid is reduced and improved viscosity and/or gel strength are obtained. Polymers of this invention can be used in drilling fluids comprising fresh or salt water, clays, weighting agents and other drilling fluid ingredients. These polymers are particularly suitable for drilling fluid additives in formations having high temperatures, salinity content and content of hardness ions, since they tend to retain their viscosity well even when aged at elevated temperatures in saline and/or hard water. In addition to use as a drilling fluid additive, the polymers of this invention can be effectively used as additives in various workover and completion fluids, e.g., for reducing the loss of a fluid pumped into a subterranean borehole, by maintaining a suitable viscosity, and improving the fluid's ability to suspend weighting agents.

When introduced into a well bore in processes for the drilling, completion or workover of wells, the polymers can be used in small amounts effective to achieve the effects desired, such as reduction of high temperature water loss, suspension of weighting agents and the like. As a general guide, the amount of polymer used will be in the range from about 0.10 to about 5, preferably 0.5 to about 2 pounds per barrel of fluid. Those skilled in the art can determine the amount of polymer to be used by suitable experiments in light of this disclosure. The polymers are useful in such applications at temperatures up to at least about 400 F. In one embodiment, the

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polymers can be added to a workover/completion fluid to provide a fluid which is substantially clay free, with a pH in the range from about 7 to about 10

The in situ polymerization embodiment of this invention is applicable to any situation wherein it is desired to selectively plug the more permeable zones in a subterranean formation by in situ polymerization of a polymer. The invention is primarily directed to the selective plugging of the more permeable zones, known as thief zones, to improve the sweep efficiency of postprimary oil recovery processes.

The preferred plug-forming materials of this invention are water-soluble, polymerizable monomers comprising an N-vinyl lactam as previously disclosed. The polymers of N-vinyl-2-pyrrolidone are presently preferred. For most applications it is presently preferred that the polymer be a copolymer produced in situ by copolymerizing the N-vinyl lactam with an unsaturated amide as previously disclosed, preferably acrylamide. Copolymers preferably contain an amount ranging from about 25 to about 75 weight percent of the N-vinyl lactam, the remainder being the unsaturated amide. For certain applications the copolymer can comprise an additional monomer, or termonomer, producing a terpolymer containing major portions of the N-vinyl lactam and the unsaturated amide in the proportions previously disclosed, with the termonomer selected from the group consisting of hydrophobic and nonanionic compounds as disclosed previously.

This embodiment of the invention preferably involves injecting into the formation a polymerization inhibitor or poison for the particular monomer(s) to be polymerized. For instance, materials to inhibit the polymerization of acrylamide, such as potassium ferricyanide, hydroquinone and the like can be injected in the formation. Polymerization inhibitors for the N-vinyl lactam can be injected into the formation in addition to or in lieu of the inhibitor for the unsaturated amide, such as for example, those selected from the group consisting of benzoquinone, nitrosobenzene and alkyl-substituted derivatives and the like. An appropriate catalyst or free radical initiator selected from the materials disclosed elsewhere herein is injected into the formation with the monomer(s) to cause polymerization in situ, as described in Example XIII. Methods for the introduction and selective removal of polymerization inhibitors for permeability correction in subterranean formations are disclosed by Barton in U.S. Pat. No. 4,190,109, issued Feb. 26, 1980, and assigned to Phillips Petroleum Company, Bartlesville, Okla.

When monomers are injected into a formation or employment in this embodiment of the invention, the amount of monomers used is not critical so long as at least an effective amount is present, and the concentration of the resulting monomer solution does not produce a viscosity so great as to cause difficulties in emplacing the monomers in the portion of the formation where they are to polymerize. The effective amount can be very small, as where the permeability of a zone is to be decreased slightly, or larger where fractures, voids, etc. are to be plugged. A concentration and amount of monomer solution should be used which will permit an effective amount of the monomers to polymerize in situ in the desired zones and have the desired effect on the permeability of those zones.

Optionally, a suitable difunctional or other multifunctional monomer such as for example divinylbenzene or

bis-methylene-acrylamide can be employed as a cross-linking agent in the process of in-situ polymerization.

The advantage obtained by using the inventive polymers through in-situ polymerization in a subterranean formation is that polymers of enhanced viscosity and stability to the effects of high temperatures, e.g. at least about 150 F, salinity and/or concentration of hardness ions are obtained when the monomers are polymerized in the presence of electrolytes, preferably a mixture of electrolytes selected from the groups of alkali metals salts and alkaline earth metal salts. Such an electrolyte solution can be introduced as the polymerization medium in the process of flushing out the polymerization inhibitor, or in certain formations the formation water can be used at least partially as the polymerization medium, with or without filtering or other treatment. The formation water and/or fluid flush material preferably have a salinity of at least about 10 grams per kilogram solution and/or a fraction of divalent hardness cations of at least about 1 weight percent, based upon the total cations. By forming a viscous and stable polymer in the more permeable zones of the formation, the permeability of the formation is made more uniform with a smaller quantity of monomers, and the permeability correction can be expected to be longer lasting.

FLOCCULATION

Other applications for the polymers of this invention include methods for concentrating finely divided organic or inorganic solids from an aqueous suspension thereof by admixing with the suspension an effective amount of the copolymer to cause accelerated sedimentation of the suspended solids and maintaining the treated suspension under quiescent conditions to separate a clarified supernatant liquid layer and a concentrated solid suspension layer.

In carrying out the flocculation embodiment of the invention, the inventive polymer is distributed in a suspension of finely divided inorganic solids in any fashion by which rapid, thorough mixing may be accomplished without excessive agitation. In a preferred method of operation, the copolymer is dissolved in water and introduced into the suspension in the form of a dilute aqueous solution. Following the introduction of the polymer solution, the treated suspension is transferred with a minimum of agitation and shearing action into a quiescent zone such as a sedimentation vessel to allow the development and settling of agglomerates of the finely divided solids. In practice, the polymer solution may be sprayed or otherwise introduced into a flume or other conduit through which the suspension is moving. In such operations the conduit may be equipped with baffle plates or other means of mild agitation at or immediately following the point of introduction of the polymer solution to assure thorough mixing. Preferably the polymer solution is added portionwise or at a plurality of sites to accomplish thorough distribution of flocculant without local overtreatment.

Following the mixing of the solution of polymer with the suspension of finely divided solids, as set forth above, the treated suspension may be submitted to various conventional procedures for the concentration or separation of solids from the suspension. For example, the treated suspension may be fed into a settling tank or thickener to effect the separation of a concentrated slurry of solids as an underflow product and a clarified aqueous effluent as an overflow product.

The amount of polymer to be employed will vary depending upon the type of inorganic solids, the degree of subdivision thereof and the rate of settling required. With highly amenable solids, such as certain chemical precipitates, excellent improvement in settling rate and clarity of supernatant liquid can be obtained when employing only 0.001 pound of polymer per ton of suspended solids. For most finely ground materials, good results can be obtained when employing about 0.01 to about 0.1 pound of polymer per ton of suspended solids, although loadings ranging up to 1 or 2 pounds of polymer per ton of solids may sometimes be required, particularly when the solids are to be filtered following treatment. In any case, an amount sufficient to increase the rate of sedimentation of the solids is employed. In some cases the inventive polymers are conveniently employed in conjunction with other flocculants such as polyacrylamides or natural polymers.

Scale Prevention

It is known to use polyacrylamide in aqueous systems to remove and/or prevent the formation of scale as shown for instance in Booth et al U.S. Pat. No. 3,463,730 (Aug. 26, 1969). However, in systems having multivalent ions and/or high temperature, polyacrylamide precipitates out after a time. The polymers described herein, however, can be used in boilers, evaporators, cooling towers, heat exchangers, and other devices where a thermal gradient exists or where areas are catalytically active and thus induce scale formation into aqueous systems. Thus in a utility of the type just described wherein the temperature and divalent metal cation concentration is above the infinite dilution line of FIG. 14, compositions described in this invention make the difference between a successful and an unsuccessful system.

The polymer can be used in the same concentrations as those polymers of the prior art, i.e., from 0.1 to 500 parts per million, preferably 1 to 20 parts per million, for instance, as disclosed in said U.S. Pat. No. 3,463,730 and for the utilities described in said patent, the disclosure which is hereby incorporated by reference. Other similar utilities for the polymers described in this invention where conditions such as high temperature and multivalent ions exist include inhibiting scale formation on the surfaces of membranes in reverse osmosis apparatuses, to fluidize and disperse insoluble alluvium deposits such as silt from water systems as for instance, deposits of silt alluvium and the like left by water systems in cooling towers, once through cooling systems and similar devices and gas scrubbers. These latter are meant to include wet scrubbers being used to clear effluent from boiler stacks, incinerator stacks, lime kilns, foundries, blast furnaces, basic oxygen furnaces, open-hearth units, coke plants, paper mill recovery boilers, pet food manufacturing facilities, electric furnaces, smelters, and asphalt plants. Another utility is aqueous hydraulic fluids under circumstances where the fluids encounter high temperatures and/or multivalent ions.

Hydraulic Fluid Viscosifier

The water soluble polymers described herein are used to thicken water-based hydraulic fluids allowing these fluids to be used directly in pumps designed for the more viscous oil-based fluids. Thickened water-based fluids also can be used at higher pressures than unthickened fluids because of the lower internal leakage in the hydraulic pump. Polymer shear stability is an important

property in this application because of the shearing nature of the pump on the fluid.

Drag Reduction Agent

The water-soluble polymers described herein are also useful as drag reducing agents. Drag reducing agents are polymeric materials that are added to flowing liquid streams to reduce friction losses. They accomplish this by reducing turbulence and increasing laminar flow in the system. Again, because the fluid will likely pass through a pump, polymer shear stability is an important attribute.

Cloud Point Measurements

When an aqueous solution of a water-soluble polymer such as an acrylamide-derived polymer is heated, it turns cloudy at higher temperature. This cloudiness disappears upon cooling and reappears as a result of additional heating. The temperature at which such cloudiness first appears is a property related to the solubility of the polymer, and is known as the cloud point. Cloud point corresponds to the lower critical solution temperature described by Billmeyer in his Textbook of Polymer Science, Second Edition (Wiley-Interscience, New York, 1971) at pages 39-43. The lower critical solution temperature is the higher temperature at which a solvent, such as water, in a given single-phase polymer-solvent system, such as PVP-Am in a synthetic sea water, is no longer a good solvent. At this temperature, the single phase system undergoes phase separation, as shown by FIGS. 2-8 in Billmeyer. Such phase separation is often marked by clouding, hazing or precipitation of the polymer. Such phase separation, and thus the lower critical solution temperature or cloud point, can be observed visually or measured by various apparatus, including turbidimetry. Since chemical modification of the polymer or solvent does not necessarily occur at or near the lower critical solution temperature, redissolution of the cloud, suspension or precipitate is noted when the temperature decreases below the lower critical solution temperature.

Apparatus has been developed in connection with the research on this invention to measure cloud points at high temperatures (up to about 325 F or even 400 F). Unless otherwise noted, this apparatus and the method described were used to determine the cloud points herein. To determine the cloud point of a given polymer with this apparatus, a solution of the polymer comprising 0.25 or 0.5 gram (as indicated) per deciliter of polymer in SSW is produced and a 35 ml aliquot of this solution is placed in a 45 ml ampule and torch-sealed under vacuum. The ampule is then placed in a protective chamber immersed in a silicone oil bath containing Dow Corning 200 Fluid. A Brinkman Model PC-801 probe colorimeter is used to supply a source of light and a detector. The light from the colorimeter is passed through a 30 inch Brinkman fiber optic light guide (No. 2023602-F) and then directed through the solution. The transmitted light is passed by another identical fiber optic light guide to the detector. The sample is heated from a temperature where the polymer solution is clear to a temperature where cloudiness exists, and is then allowed to cool. For example, to measure cloud points in the range of about 250-275 F, the silicone oil bath containing the ampule is heated from 200 F to 280 F and cooled back to 200 F in approximately one (1) hour with the heating cycle taking about 30 minutes. Use of a pressure cell allows going to 400 F. To detect the

onset of cloudiness, the absorbance of the polymer solution is measured and recorder (on a strip chart recorder) as a function of temperature for the heating-cooling cycle (Absorbance is outputted by passing the transmittance signal through a logarithmic amplifier and on to the recorder.) The average of the temperatures at which the first trace of cloudiness appears and the last trace of cloudiness disappears employing the above described apparatus and method is the numerical average cloud point temperature, hereinafter "cloud point," as that term is used in the specification and claims unless otherwise indicated. This measurement appears to be quite reproducible to within $\pm 3\%$ with the apparatus presently in use.

It has been noted that the cloud points of the copolymer solutions of this invention can be correlated with desirable properties comprising the resistance of the copolymers to high temperatures. Generally speaking, the higher the cloud point of the freshly-prepared polymer, the higher the temperature (which can be as much as about 50 F or more (but generally no more than 10 F above the cloud point) which the copolymer can be expected to withstand without suffering a significant loss in its capacity to impart viscosity to the test solution. See Example V. Furthermore, tests to determine cloud point after aging can be used to indicate the prospects of the copolymers withstanding further aging under such conditions, or under less severe conditions. As shown in FIG. 5 and discussed in Example VI, although the cloud points measured for copolymer samples aged at different temperatures initially vary, as aging exceeds about 20 days, the cloud points approach a common equilibrium value. This equilibrium value is believed to be an excellent indicator of the copolymer's resistance to degradation (precipitation) at high temperatures.

The VP-Am copolymers and terpolymers of this invention hydrolyze. As is known, hydrolysis of an amide alters the amide functionality to an acid (or its salts). In the case of acrylamide, acrylic acid or its salts are formed. In the case of polyacrylamide or its copolymers, including VP-Am, the polymer is altered to contain monomer units of carboxylic acids or their salts, thus introducing ionic character to the polymer. The degree of hydrolysis has been found to increase to a maximum equilibrium value of about 70 to 80 percent at 250 F based on the acrylamide content. It has been noted that the cloud point temperature also changes over the same time frame and equilibrates. The inference is that the cloud point temperature reflects the basic polymer nature, and that the stability of the equilibrium cloud point temperature (corresponding to the stability of the degree of hydrolysis of the copolymer) probably indicates a constant polymer makeup.

The utility of cloud point measurements as predictors of the performance and/or stability of polymer compositions in high temperature environments is disclosed in U.S. Pat. No. 4,016,932, which states that in surfactant systems for oil recovery comprising at least one anionic and at least one nonionic surfactant, superior results are obtained when the nonionic surfactant is chosen to have a cloud point slightly above the formation temperature. Similarly, measurement of this invention, before and/or after aging at elevated temperatures, facilitates the selection of polymers which will provide superior performance and stability for the various applications disclosed herein. For the best prediction of polymer performance, it is preferred that the cloud points be deter-

mined in aqueous solutions similar to the proposed environment for employment, e.g. in salinity and hardness, and at standardized concentrations of the polymer. For use in enhanced oil recovery in hot saline formations, for example, polymers having cloud points in brine of at least as high as the formation temperature after short-term aging at elevated temperature are preferred. Since long-term viscosity stability at high temperatures is required in enhanced oil recovery, and since polymers having relatively high cloud points after aging correlate well with polymers having such stability, polymers with relatively high cloud points are preferred for use in enhanced oil recovery processes. Conversely, polymers used in drilling fluids and the like are subjected to high formation and/or well bore temperatures, salinity and hardness ions for shorter periods of time. Thus, polymers with cloud points relatively lower with regard to formation and/or well bore temperature than those required in polymers selected for, e.g., enhanced oil recovery, can be utilized in drilling fluids, etc. For example, a polymer with a cloud point somewhat lower than the maximum formation and/or well bore temperature may perform adequately and retain the desired properties such as viscosity for a period of use limited to weeks, days or even hours. This is particularly important when drilling or servicing deep and/or hot wells, such as geothermal wells.

Based on the relatively stable properties of the polymers suitable for use in the processes of the invention after short-term heat aging, for applications where maximum stability in hot, saline environments is desired, the polymers can be pre-aged or hydrolyzed before use. That is, the polymers are hydrolyzed in solution by heat aging at a suitable temperature until an equilibrium value of hydrolysis is attained. The aging temperature must be less than the decomposition temperature of the polymer. The polymers can be aged in any available aqueous medium, but media similar to the environments in which the polymers are to be employed are presently believed to produce optimum results. Since the aging time and temperature are interdependent, to fully stabilize polymer properties such as viscosity, the polymers must be aged for long enough at the temperature selected to produce an equilibrium degree of hydrolysis. The polymers can also be at least partially hydrolyzed by treatment in solution with a base, an acid, a polyacid such as polyacrylic acid, a polyelectrolyte such as polyvinylpyrrolidone or an electrolyte such as an alkali or alkaline earth metal salt.

The degree of hydrolysis can be tested directly by the Dow Color Test, as described in Example VII herein, or can be estimated by the equilibrium cloud point temperature, as described in example VI. The minimum temperature suitable for this pre-aging is a temperature high enough to produce a hydrolysis rate which allows pre-aging to be completed in a reasonable time. As seen in FIG. 6, temperatures of at least about 150 F, preferably in the range of about 250 F to about 300 F should generally produce suitable hydrolysis rates for the inventive polymers. Temperatures higher than 300 F can be used, provided suitable equipment is available and the decomposition temperature of the polymer is not exceeded. In the production and pre-aging of a given polymer, the relationship between the times and temperatures appropriate for pre-aging can be readily determined. When a temperature of at least about 250 F is used, the polymers are preferably aged for at least about 7 days.

The invention is further illustrated by the following examples, which should not be regarded as more limiting than the appended claims. Unless otherwise noted, all percentages and/or parts are by weight.

EXAMPLE I

Copolymer Preparation and Testing

The polymer preparations were carried out in 10 ounce crown top glass beverage bottles. Each bottle was charged under an inert atmosphere with 20.0 g total of the monomer(s), 200.0 g of the reaction medium (t-butyl alcohol, distilled water, water containing salts or SSW, as specified) and 0.02 g of initiator, or the specified amount in terms of weight percent, based on the total monomer weight and desired solution viscosity. Each bottle was purged for about 10 to 20 minutes with an argon stream to remove oxygen and capped. The SSW was prepared as described earlier.

The bottles were placed in a bath maintained at 50° C. and rotated for at least 4 hours to achieve substantially complete polymerization of the monomers. The bottles were removed and the resulting solutions in aqueous media were diluted with the specified test medium to obtain the desired viscosities for the tests. Polymers prepared in t-butyl alcohol were separated from the alcohol medium by elutriation, then diluted with the test media for viscosity tests.

Aging of the samples were conducted in torch-sealed glass ampules containing about 30 to 35 mL of polymer solution, e.g., 2 weight percent or as specified in the Tables, in an oven maintained at the specified temperature. At various time intervals, ampules were removed, observed for any evidence of precipitation and cooled to room temperature. Each seal was broken and the viscosity of the solution as a function of shear rate was measured at 77 F (ambient room temperature) with a Brookfield LVT model viscometer equipped with an UL adapter for viscosity measurements at different shear rates. Each viscosity listed is an average of three measurements at each shear rate.

Screen factors, when reported, were determined by measuring the time required for passage of an aliquot of aqueous polymer solution by gravity flow through five 100-mesh stainless steel screens, and dividing this time by the time required for passage of the same amount of solvent through these screens under identical conditions. Screen factors are related to viscosity of the polymer solution, thus the higher the factor the higher the viscosity. The test method is detailed by Foshee, W. C., Jennings, R. R. and West, J. J. in Paper SPE 6202 entitled "Preparation and Testing of Partially Hydrolyzed Polyacrylamide Solutions" presented at the 51st Annual Fall Meeting of the Society of Petroleum Engineers in New Orleans, Oct. 3-6, 1976.

In Table IV, footnote f, the cloud point was visually estimated with an aged sample tested at an elevated temperature by placing the ampule containing the polymer in another bath maintained at a lower temperature, so that the polymer solution was cooled sufficiently to allow redissolving of the precipitated polymer. The bath temperature was then slowly raised and the temperature at which cloudiness visually reappears was recorded as the cloud point. For example, the cloud point of a polymer solution aged at 250 F that had become cloudy was determined to be 215 F (see footnote f, Table IV) by cooling the hot mixture to about 180 F, thus allowing the precipitated polymer to redissolve. The temperature was slowly raised until 215 F was reached, at which point the cloudiness visually reappeared. This temperature was recorded as the cloud point.

As discussed earlier, it has been found that cloud point can be correlated with the maximum temperatures at which such polymers can be expected to retain their viscosity when aged. Thus, newly-formulated polymers can be quickly evaluated as to their suitability for laboratory or field tests for retention of viscosity under aging at elevated temperatures.

The viscosities of the aged polymers are listed in Table I.

TABLE I

Aging Results For Homopolymers and Copolymers of N-Vinyl-2-Pyrrolidone and Acrylamide Prepared in SSW with 0.5 Weight Percent AIBN¹ and Different Monomer Ratios and Aged in SSW

Sample	Weight Percent Concentration in			Days aged	Brookfield ² Viscosity, centipoise after aging at	
	VP	Am	SSW		200 F	250 F
1 (homopolymer)	100	0	2.0	0	16.1	16.1
				21	14.2	13.8
				48	14.0	13.6
				125	— ^b	— ^b
				124	— ^b	— ^b
2 (copolymer)	87.5	12.5	2.0	0	33.4	33.4
				21	60.1	61.9
				48	60.5	60.9
				124	— ^b	— ^b
				120	— ^b	— ^b
3 (copolymer)	75	25	2.0	0	46.8	46.8
				17	42.9	42.8
				44	43.0	41.9
				120	— ^b	— ^b
				120	— ^b	— ^b
4 (copolymer)	62.5	37.5	2.0	0	108.4	108.4
				27	124.9	105.0
				48	129.0	117.0
				105	127.0	112.0
				120	— ^b	— ^b
5 (copolymer)	50	50	2.0	0	331	331
				26	457	478
				47	476	386
				119	— ^b	— ^b
				119	— ^b	— ^b
6 (copolymer)	37.5	62.5	2.0	0	860	860
				24	1934	1376

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TABLE I-continued

Aging Results For Homopolymers and Copolymers of N Vinyl-2-Pyrrolidone and Acrylamide Prepared in SSW with 0.5 Weight Percent AIBN ¹ and Different Monomer Ratios and Aged in SSW						
Sample	Weight Percent		Concentration in SSW	Days aged	Brookfield ² Viscosity centipoise, after aging at	
	VP	Am			200 F	250 F
7 (copolymer)	25	75	2.0	45	1686	1038 ^c
				101	1624	910 ^d
				117	— ^e	— ^e
				0	1330	1330
				20	>2000	1220 ^f
				43	>2000	813 ^f
				99	1983	142 ^f
8 (copolymer)	12.5	88.5	2.0	113	— ^e	— ^e
				0	>2000	>2000
				20	>2000	>1857 ^f
				42	>2000	660 ^f
				100	>2000	650 ^f
9 (control)	0	100	0.4	112	— ^e	— ^e
				0	19.1	19.1
				4	3.0 ^h	2.1 ^h
				18	—	1.4 ^h
				56	24.4 ^h	1.3 ^h
				87	1.3 ^h	1.6 ^h

Notes
^aClear aging containing
^bHeavy very small amount of precipitate, test continuing
^cCloudy at 250 F., clear at 78 F
^dVery heavy white precipitate At 78 F., clear with a little floating material.
^eVery heavy with white precipitate on ampule sides, test continuing
^fVery cloudy with much white precipitate on ampule side. At 78 F., clear with clear gel
^gVery cloudy with much white precipitate on ampule side, test continuing.
^hClear with powdery white precipitate at aging temperatures and at 78 F
ⁱAcrylamide/acrylonitrile, based on weight of monomers
^jDetermined at shear rate of 7.3 sec⁻¹ or lower at 25 C. (e.g. 7.1, 3.7 and 1.8 sec⁻¹) in terms of centipoise (cP).

The aging results presented in Table I show that the invention VP and VP/Am polymers are more thermally stable under the test conditions at 200 F than the polyacrylamide control. The solution viscosities of the copolymers generally increase with increasing Am content. The lower solution viscosities of sample 3, 75/25 VP/Am, compared with those of sample 2, 87.5/12.5 VP/Am, are believed to be anomalous, since later work shows viscosity results intermediate to those of samples 2 and 4 of Table I. The various copolymers, however, show consistently good thermal stability in this test.

The higher the level of Am in the copolymer, the greater the probability of precipitation at a test temperature of 250 F. For example, when the Am level is higher than about 75 weight percent, precipitation occurs at some time less than about 20 days. When the Am level is lower than about 65 weight percent, the results show much less to no precipitation occurring, even after up to about 125 days at 250 F. Based on both the viscosity and the stability results, the data in Table I indicate that suitable copolymers for EOR have VP/Am levels ranging from about 60/40 to about 40/60 at the temperatures tested. Such copolymers provide reasonably viscous solutions at relatively low polymer concentrations which are very resistant to thermal degradation. The higher proportions of VP are generally preferred for use in reservoirs having more "hostile" conditions, e.g., higher temperature, salinity and hardness of the formation water.

TABLE II

Viscosity of 2 Weight Percent Solutions of 50:50 VP-Am Copolymers Prepared with Different Initiators in Distilled Water and Diluted in SSW			
Run No	Initiator		Brookfield Viscosity ^b cP
	Description	Weight Percent ^a	
1	AIBN ^c	1.0	157
2	"	0.5	226
3	"	0.25	233
4	"	0.13	280
5	t-BPP ^d	1.0	11.2
6	"	0.5	52.3
7	"	0.25	42.8
8	"	0.13	49.7

^aBased on weight of monomers.
^bName as described in footnote k of Table I
^cazobisisobutyronitrile
^dtert-butylperoxypivalate

TABLE III

Viscosity of 2 Weight Percent Solutions of 50:50 VP-Am Copolymers Prepared with Different Initiators in SSW and Diluted in SSW			
Run No	Initiator		Brookfield Viscosity ^b cP
	Description	Weight Percent ^a	
1	AIBN ^c	1.0	530
2	"	0.5	657
3	"	0.25	>2000
4	"	0.13	>2000
5	t-BPP ^d	1.0	17.4
6	"	0.5	15.4
7	"	0.25	19.8
8	"	0.13	24.4

^aBased on weight of monomers.
^bName as described in footnote k of Table I
^cazobisisobutyronitrile
^dtert-butylperoxypivalate

The results in Tables II and III show rather dramatically that the viscosities of the polymers prepared in SSW with AIBN are substantially higher in comparison to the viscosities of corresponding polymers, prepared in water using AIBN initiator. It is also clear from the data that AIBN is preferred over the t-BPP as the initiator, based on the much higher polymer solution viscosities obtained. The data in Tables II and III also show that the viscosities of polymers prepared with an AIBN initiator or inversely proportional to the amount of initiator employed, as would be expected by those skilled in the art. This trend is not consistent in the polymers prepared with t-BPP, suggesting that some interaction may take place between the polymer produced and the t-BPP in the solution.

TABLE IV

Aging Results for Several 50:50 PV-Am Copolymers Prepared in SSW or t-Butyl Alcohol and Aged in SSW at 200 F						
Sample No	Reaction Medium	Initiator		Copolymer		Brookfield Viscosity ^d cP
		Description	Weight Percent ^f	Concentration Wt %	Days Aged	
1 ^b	SSW	AIBN	1.0	2.0	0	530
					28	670
					54	664
					111	719
					320	— ^c
2 ^c	SSW	AIBN	0.13	0.5	0	19.5
					28	28.0
					61	28.6
					98	— ^c
3 ^d	SSW	t-BPP	0.25	2.0	0	19.8
					35	23.5
					94	26.8
					190	— ^c
4	t-butyl alcohol (TBA)	t-BPP	1.0	2.0	0	18.6
					32	27.0
					63	27.0
					173	27.8 ^e

Notes
^aSame as described in footnote^a of Table I
^bSame polymer as in run 1, Table III
^cSame polymer as in run 4, Table III
^dSame polymer as in run 7, Table III
^eClear solution in a parallel test at 250 F., test continuing.
^fTested at 250 F. The Polymer solution became cloudy after 13 days at 250 F. The cloudiness disappeared on cooling to room temperature and apparently did not affect solution viscosity. The cloud point was determined to be 315 F.
^gBased on weight of monomer.

The data given in Table IV show typical results obtained with 50:50 PV-Am copolymers prepared in SSW or t-butyl alcohol and aged at 200 F or 250 F. Sample 1 has been aged for over 1467 days at 250 F with clear solutions obtained, indicating the exceptional stability of the polymer in a saline hard water environment under the test conditions employed. Since t-BPP is believed to interact with the polymer produced, it would not be appropriate to draw any conclusions from the results of samples 3 and 4.

EXAMPLE II

50:50 VP-Am Copolymers Prepared by Gamma-Irradiation

A series of 50:40 weight percent VP-Am copolymers was prepared by gamma-irradiation. A 20 weight percent solution of monomers in distilled water (control runs 1, 3 and 5) or synthetic sea water (SSW) (inventive runs 2, 4 and 6) were irradiated at room temperature, e.g. 25° C. Each sample, containing water and monomers, weighed about 15 g. The dosage rate was 600 kilorads per hour. The nature of the polymerization media, irradiation times and results obtained are given

in Table V. The SSW was prepared as disclosed in earlier

TABLE V

Sample No	Gamma Irradiation of VP-Am Solutions at 25° C.			
	Polymerization Conditions			
	Medium	Time Minutes	Dosage KRads	Description of Polymerized Mixture
1	H ₂ O	60	600	Clear soft gel-like
2	SSW	"	"	Yellow, soft gel-like
3	H ₂ O	90	900	Clear stiff gel
4	SSW	"	"	Yellow stiff gel
5	H ₂ O	30	300	Clear very thick solution
6	SSW	"	"	Yellow easily flow solution

Samples 5 and 6 apparently did not receive enough

radiation to give polymers of sufficient molecular weight to provide desirable solution viscosities when diluted. Nor further testing of these samples was done. However, 14 g portions of samples 1 to 4 were individually admixed with 266 g portions of water or SSW, corresponding to the polymerization medium employed, to produce solutions containing 10 weight percent polymer, with each mixture placed in a closed container and tumbled for 4 days. It was noted that samples 1 and 2 completely dissolved to give solutions 1A and 2A, each containing about 1 weight percent solids. Samples 3 and 4 contained crosslinked gel suspended in the solution and were deemed to have received an overdose of radiation. No further testing of these was done.

The viscosities of solutions 1A and 2A were determined with a Brookfield viscometer provided with a U.L. Adaptor at 6 RPM and 24° C. Solution 1A had a viscosity of about 46.5 cp and solution 2A had a viscosity of about 38.8 cp, which under the conditions employed are considered comparable.

The above results demonstrate that the copolymers of this invention can be prepared in SSW by gamma-irradiation.

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EXAMPLE III

Inherent Viscosities of 50:50 VP-Am in Various Media

Viscosities of the polymer solutions disclosed in the examples herein have been expressed variously as Brookfield viscosity, relative viscosity, inherent viscosity, intrinsic viscosity or specific viscosity. Definitions and discussions of these terms can be found in Example VIII or "Viscometry," Encyclopedia of Polymer Science and Technology, Vol 14, pp 717-22 (John Wiley & Sons, New York, 1971), and in J. R. Fried, "Molecular Weight and its relation to properties," Plastics Engineering, August, 1982, pp 27-30.

A series of 50:50 (by weight) VP-Am copolymers was prepared as before by solution polymerization at 50° C using about 0.1 g (0.50 weight percent based on total components) AIBN as initiator, 10 g each of VP and Am and 200 g of polymerization medium. The polymerization media employed ranged from distilled water to water containing one or more dissolved salts as indicated below. The Ionic Strength (I.S.) of each solution containing a dissolved salt or salts was about 0.7, the I.S. of SSW.

Each polymerization run was conducted overnight, e.g. about 15 hours. The inherent viscosity of each copolymer solution containing 9.1 weight percent copolymer was determined by means of an Ubbelohde viscometer at 25° C in distilled water and in water containing one or more dissolved salts.

The results are given in Table VI

TABLE VI

Inherent Viscosity of 50:50 VP-Am in Various Media All Salt-Containing Media at 0.7 Ionic Strength							
Run No.	Polymer Medium	Inherent Viscosity Medium Inherent Viscosity, dL/g ^a , 25° C					
		Water	SSW	NaCl/MgCl ₂	NaCl	CaCl ₂	MgCl ₂
1	Water	5.4	5.7	—	5.2	5.6	5.6
2	SSW	7.0	7.3	6.9	7.1	7.1	7.2
3	NaCl aq	6.5	6.7	6.5	6.8	6.6	6.6
4	CaCl ₂ aq	6.3	6.5	6.3	6.5	6.4	6.3
5	MgCl ₂ aq	6.4	6.5	6.4	6.5	6.4	6.4
6	NaCl/MgCl ₂ aq ^b	6.7	6.8	6.2	6.5	6.3	6.1

^aAll samples for inherent viscosity measurements were at 0.05 weight percent total solids. Each value in the table is the average of three determinations. Reproducibility was within about 0.1 deciliters per gram.
^b1.96:1 weight ratio NaCl/MgCl₂. Prepared by mixing equal volumes of 0.7 I.S. NaCl and 0.7 I.S. MgCl₂
aq = aqueous

The inherent viscosity results for the 50:50 VP-Am copolymer prepared in SSW of 0.7 I.S. are consistently higher than those prepared in the other polymerization media employed. Generally, the copolymers prepared in such media exhibited about the same viscosity results regardless of the inherent viscosity media chose for their determinations. While the inventive polymers prepared in SSW or mixed electrolyte media have higher viscosities, polymers prepared in the other media can be used in certain process embodiments of this invention.

EXAMPLE IV

Effects of Heat Aging on Viscosities

Several 50:40 VP-Am copolymers were prepared at 50° C. in the manner previously described using 0.25 weight percent AIBN as the initiator in an aqueous polymerization medium as follows. Polymer A was prepared in distilled water. Polymer B was prepared in 0.7 I.S. NaCl solution. Polymer C was prepared in 0.7 I.S. SSW. A portion of each polymer was diluted to the

0.25 weight percent polymer level in the same medium employed in its preparation.

Each diluted polymer solution was divided into 2 portions to give 6 test samples in all. In series 1, the three dissimilar unaged polymer solutions were individually tested to determine how solution viscosity changed over the temperature range of about 80 to 300 F. In series 2, the three dissimilar polymer solutions were aged for 7 days at 300 F in an essentially oxygen-free atmosphere.

Aliquots of each polymer solution were passed through a capillary viscometer, a 40 foot length of 0.069 inch inner diameter stainless steel tubing. The solution viscosities, in terms of centipoise (cP), were calculated from the viscometer results by applying the Poiseuille equation as known in the art.

The viscosity results obtained for unaged polymers are tabulated in Table VII and shown in FIG. 1, results for the aged polymers are tabulated in Table VIII and shown in FIG. 2. The results obtained with the unaged polymers, shown in FIG. 1 as curves A, B, and C show that they have significantly greater solution viscosities than does SSW containing no polymers, shown in FIG. 1 as curve D, over the 80 to 300 F temperature span tested (Curve D was drawn from the properties of SSW listed in Table IX.) The polymers prepared in either saline, I.S. of 0.7, (curve B) or SSW, I.S. of 0.7, (curve C) have significantly greater viscosities than does the polymer prepared in distilled water (curve A) over the entire temperature range tested.

The results obtained with the polymer aged for 7 days at 300 F are shown in FIG. 2. They indicate again that all of the polymers (curves A, B, C) have greater solution viscosities than does SSW (curve D) over the temperature range tested.

The results also show that polymers prepared (curve C) in SSW are substantially more resistant to the effects of heat than polymers prepared in saline (curve B) or in distilled water (curve A), based on their significantly greater solution viscosities over all temperatures in this test. However, even the polymers prepared in saline or distilled water are potentially useful in certain process embodiments of this invention.

As shown in FIG. 2, the viscosities of all the polymers prepared approach that of SSW above 300 F. However, it should be noted that even at these temperatures the polymers are present as homogeneous solutions. In contrast, other polymers such as polyacrylamide precipitate as solids at about 200 F or below. Furthermore, the viscosity of the inventive VP-Am

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copolymers relative to that of SSW at 200 F can be increased by using higher concentrations of the copolymers, and/or copolymers of higher molecular weight

EXAMPLE V

Cloud Points and Viscosity

TABLE VII

Unaged Polymers					
Polymerized in Distilled Water		Polymerized in NaCl		Polymerized in SSSW	
Temp (F)	Visc (cP)	Temp (F)	Visc (cP)	Temp (F)	Visc (cP)
85	2.35	81	4.32	83	4.39
98	2.17	90	4.17	89	4.25
110	1.91	103	3.81	100	3.71
117	1.74	110	3.57	113	3.49
124	1.61	123	3.05	119	3.22
136	1.33	129	2.82	133	2.76
147	1.23	142	2.44	139	2.52
159	1.14	148	2.19	152	2.22
166	1.07	161	1.93	158	2.03
179	0.97	167	1.88	171	1.74
185	0.91	180	1.67	177	1.70
196	0.83	193	1.47	189	1.52
204	0.80	199	1.40	202	1.41
217	0.73	212	1.26	209	1.46
224	0.70	219	1.21	222	1.19
237	0.65	232	1.13	229	1.15
244	0.61	245	1.01	242	1.02
256	0.58	251	0.97	253	0.93
269	0.55	264	0.89	260	0.92
275	0.53	277	0.84	273	0.82
288	0.51	289	0.79	292	0.76
300	0.49	302	0.75	305	0.72

TABLE VIII

Aged Polymers					
Polymerized in Distilled Water		Polymerized in NaCl		Polymerized in SSSW	
Temp (F)	Visc (cP)	Temp (F)	Visc (cP)	Temp (F)	Visc (cP)
88	1.34	80	2.81	84	4.36
96	1.33	95	2.72	96	4.62
109	1.12	107	2.38	108	3.28
123	0.99	119	1.99	119	3.35
135	0.87	132	1.71	131	2.99
147	0.78	145	1.46	145	2.44
160	0.68	157	1.27	157	2.07
174	0.62	170	1.08	170	1.70
182	0.56	183	0.93	184	1.45
200	0.50	196	0.80	197	1.26
212	0.47	209	0.70	209	1.02
226	0.43	221	0.59	221	0.89
239	0.38	233	0.53	234	0.75
251	0.37	246	0.47	247	0.64
264	0.33	258	0.40	259	0.51
277	0.31	270	0.34	271	0.41
289	0.28	282	0.30	284	0.34
300	0.26	301	0.25	303	0.29

TABLE IX

SSW Viscosities	
Temperature F	Viscosity (cP)
80	0.85
100	0.69
120	0.58
140	0.50
160	0.435
180	0.375
200	0.34
220	0.31
240	0.28
260	0.26
280	0.245
300	0.23

A series of VP/Am copolymers having VP/Am weight ratios of 90/10, 80/20, 70/30, 60/40, 55/45, 50/50 and 45/55 as before was prepared as before in 0.7 I S saline with 0.256 weight percent AIBN (based on the total monomer) as the initiator. A portion of each polymer solution was diluted to 0.25 weight percent copolymer in 0.7 I S SSW in series A and to 0.50 weight percent copolymer in 0.7 I S SSW in series B. The series A solutions were subsequently aged for 1 week at 300 F in the absence of oxygen and the polymer viscosity of each solution determined at 300 F using a capillary viscometer as previously described. The series B solutions were divided into two portions. Portion 1 was aged for 7 weeks in SSW at 250 F in the absence of oxygen. Portion 2 was aged in SSW at 300 F for 7 weeks in the absence of oxygen. The cloud point of each solution in series B was determined in the manner previously described.

The series A viscosity results are shown in FIG. 3, plotted as polymer viscosity/SSW viscosity ratio vs. copolymer composition. The series B cloud point results are plotted in FIG. 4. The viscosity results indicate that the most viscous polymer solutions were obtained at VP/Am weight ranges varying from about 80/20 to about 50/50. The optimum range, with these polymers as the basis, appears to be about 65/35 to about 55/45, with 60/40 giving the best results. Although copolymers prepared in synthetic sea water should be more viscous, the optimum range of monomer proportions should be similar to that obtained here.

The cloud point results plotted in FIG. 4 indicate that the most degradation-resistant copolymers are formed with a VP/Am weight range varying from about 90/10 to about 55/45. That is, the cloud point varied from about 295 F for 55/45 PVP/Am copolymer to about 300 F for the 90/10 VP/Am copolymer. However, the peak cloud point temperature, for the 60/40 copolymer, was above 325 F, the limit of the apparatus used for that run, for the sample aged at 250 F. These results, in light of the highest solution viscosity results obtained with heat-aged 60/40 copolymer (FIG. 3), suggest that this copolymer is about optimum in composition for EOR applications in reservoirs with temperatures at least about 250 F. On the other hand, the results obtained at 300 F suggest that copolymers having about equivalent performance can be expected when the VP/Am weight ratios vary from about 70/30 to about 60/40. As noted above, although copolymers prepared in synthetic sea water should display superior viscosity and stability, the optimum ranges of monomer proportions should correspond to those determined here.

Generally, better results were obtained with the copolymers aged at 300 F (except for the 60/40 copolymer) than at 250 F. The degree of hydrolysis appears to stabilize at about 80% Am hydrolyzed. At 80% Am hydrolyzed the VP-Am (aged) sample is completely soluble in SSW at the temperatures below the cloud point. This equilibrium value, or consistency of degree of hydrolysis with time, permits a safe prediction that the polymer properties, specifically solubility and viscosity, will not change appreciably with time.

The viscosities and cloud points obtained for copolymers prepared in saline solution indicate that such copolymers would be useful in certain process embodiments.

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ments of this invention, even if not as viscous or stable as copolymers prepared in synthetic sea water

EXAMPLE VI

Equilibrium Cloud Points

A 50/50 (weight ratio) VP/Am copolymer was prepared as before in 0.7 IS SSW using 0.125 weight percent AIBN (based on the total monomer) as the initiator. The polymer solution was diluted with SSW to obtain a solution containing 0.5 weight percent copolymer. Individual portions of the diluted copolymer solution were aged for the specified time at the specified temperatures (250 F, 280 F and 300 F) in the absence of oxygen, and the cloud point of each copolymer solution determined as previously described. The results obtained are plotted in FIG 5

The curves indicate that the cloud point temperatures decline, e.g., perhaps (25-30 F, in the first 10 days aging, regardless of the aging temperature. The copolymer solution exposed to the highest temperature, 300 F, showed the steepest decline. After about 10-15 days, however, the cloud point temperatures of samples aged at the higher temperatures remained about the same for the duration of the test, e.g., 25 days. The cloud point temperatures thus appear to stabilize at an equilibrium value of about 260-270 F, whether tested at 250, 280 or 300 F, indicating that the copolymer should be resistant to degradation in hot, saline environments at temperatures at least as high as the equilibrium cloud point temperature.

EXAMPLE VII

Hydrolysis of the Copolymers

As mentioned earlier herein, the equilibrium cloud points and resultant properties of the aged copolymers are believed related to the degree of hydrolysis of the copolymers. Selected samples of the copolymers were tested for degree of hydrolysis by the Dow color test, described more fully by Foshee, et al, in Paper SPE6202 (New Orleans, 1976), previously cited. To determine the percent hydrolysis, the concentration of amide surviving the hydrolysis is determined by an iodometric method, converting the amide groups to N-bromoamide, followed by a reaction with potassium iodide to form iodine which is then complexed with starch. The amount of this iodine-starch complex is then spectrophotometrically measured. The degree of hydrolysis can also be determined by the titration of amonumions produced as a result of the hydrolysis with sodium hydroxide, but the Dow color test has been found to be more convenient and sufficiently accurate. In FIG 6, the effect of aging in SSW on the degree of hydrolysis of a 0.5 weight percent solution of a 50:40 PVP-Am copolymer prepared in SSW is plotted for three different aging temperatures. It is apparent that the hydrolysis process is relatively slow when the polymer is aged at 200 F but exceeds the 50 percent point after about 15 days at 250 F. When the copolymer is aged at 300 F, 40 percent hydrolysis is attained almost immediately, and 60 percent is exceeded within ten days. However, as seen in FIG 7 and as described earlier herein, these copolymers tend to attain an equilibrium degree of hydrolysis eventually, no matter what the aging temperature. As seen in FIG 7, samples of a 0.5 weight percent 50:50 copolymer of VP-Am prepared in SSW and aged in SSW at the temperatures of 250, 280 and 300 F all

attain a percent hydrolysis in the range from about 65 to 75 percent after about 15 days aging

EXAMPLE VIII

K Values as Indicators of Relative Viscosity and Molecular Weight

Fikentscher K values were developed to relate the relative viscosity of any polymer solution to concentration, and as functions of molecular weight of the polymers. This K equals $1000 k$, where k is given by "Fikentscher's formula",

$$\frac{\log \eta_{rel}}{C} = \frac{75 k^2}{1 + 15 kC} + k$$

where C is concentration in grams per deciliter solution. The development and uses of these K values are described by K. H. Meyer in "Natural and Synthetic High Polymers", pp 24-25 (Interscience, New York, 1942) and Schuldnecht in "Vinyl and Related Polymers", p. 676 (John Wiley & Sons, New York, 1952).

The relative viscosity (viscosity ratio), η_{rel} , is the ratio t/t_0 , which can be determined from the average efflux times measured for the solution, t , and for the solvent, t_0 .

With sufficiently long efflux times, e.g., about 100 seconds or longer, the specific viscosity, η_{sp} , can be determined from the relationship

$$\eta_{sp} = \frac{(t - t_0)}{t_0}$$

(Generally, for the solutions employed, the value η_{sp} is determined by subtracting 1 from η_{rel} .)

The ratio, η_{sp}/C , is called the reduced viscosity (viscosity number).

The intrinsic viscosity can be determined by plotting reduced viscosity vs concentration and extrapolating to measure the intercept for zero concentration.

For greater detail, see ASTM D 2857 and/or Polymer Technology—Part 3, pages 27-33, Plastics Engineering, August 1982.

K values have been used for years to describe the viscosity grades of commercially marketed cellulose polymers as well as polyvinylpyrrolidones and other polymers. The use of K values has become well established and is retained as a means of expressing relative molecular weight, for example, K values for solutions of homopolymers of vinyl alkyl ethers are reported in Kirk-Othmer, *Encyclopedia of Chemical Technology*, Second Edition, Volume 21, pp 419-420. As previously discussed herein, U.S. Pat. No. 3,500,925 discloses and claims homopolymers and copolymers of N-vinyl lactams, including N-vinyl-2-pyrrolidone, having K values of 10 to 140. Fikentscher, et al disclose in U.S. Pat. No. 3,006,900, issued Oct. 21, 1961, copolymers of methacrylamide and N-vinylpyrrolidone, and "mixed copolymers" including at least one other monomer such as acrylamide, characterized by K values of at least about 35.

Examples of inventive and control copolymers of 50:40 VP-Am composition were prepared by methods disclosed herein, tested for relative viscosity (η_{rel}), and characterized by K values calculated in accordance with the above formula.

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Relative Viscosity Measurement

Relative viscosities (η_{rel}) of the VP-Am copolymers were determined by comparing the flow time of polymer solution at a given polymer concentration with the flow time of the heat solvent. The following relationship of flow times describes Relative Viscosity

$$\eta_{rel} = \frac{t}{t_0} = \frac{\text{flow time polymer solution}}{\text{flow time of heat solvent}}$$

In all examples herein, relative viscosity was measured in an Ubbelohde #1 capillary viscometer at 25.0° C. Flow times were taken by stop watch, and the times recorded in most cases to the nearest 1/100th second or in all cases to the closest 1/10th second. The precision of this time measurement was assured by repeating each flow through the viscometer three times, and an average flow time, from a range of values of no more than 2/10th second, reported.

Based upon the precision of these and other measurements, the precision of the calculated K values is estimated to be $\pm$ less than about one K value unit.

Surprisingly, the K values calculated for even copolymers prepared in a distilled water polymerization medium were higher than those reported in U.S. Pat. No. 3,500,925, and the K values for copolymers prepared by the inventive methods disclosed herein were substantially higher. Over the ranges tested, the K values were found generally to vary inversely with polymer concentration in the test solution, e.g., the lower the concentration, the higher the K value. Some variation was also found depending upon the nature of the solution in which the polymers were tested for relative viscosity before calculating the K values. For polymers prepared in the same polymerization media, measurement of relative viscosity in synthetic sea water (SSW) generally produced higher K values than for those tested in H₂O, with polymers tested in a solution of mixed salts producing K values lower than the synthetic sea water but slightly higher than solutions of NaCl.

FIG. 8 describes the variation of the K value with the polymer concentration in test solution for copolymers prepared in water. Since it was indicated in some sources in the literature that measurements for K values were made with a concentration equal to 1.0 g per deciliter of solution, one of these samples was tested in water at this concentration and a K value of (b) 141.8 was obtained for it. In these aqueous systems, the concentrations in grams/deciliter and weight percent are approximately equal. Identical samples were tested in various electrolyte solutions at concentrations of 0.5 g/dL and below. As can be seen in FIG. 8, the K values obtained were generally higher than those calculated for samples tested in water at the same concentrations. The maximum values were seen for samples tested in synthetic sea water, with K values ranging from 149 to 176; samples tested in water produced K values 3 to 5 units lower. For clarity, only the values for samples tested in SSW and H₂O have been plotted, with all data listed in Table X. Those samples tested in saline solution produced K values ranging from 150 to 179, with samples tested in solutions of magnesium chloride and calcium chloride producing K values slightly below these figures.

Samples of VP-Am (50-50) copolymer were also prepared in SSW and tested in SSW for comparison with the copolymers prepared in water. The results of rela-

tive viscosity measurements and calculated K values are tabulated in Table XI. The K values for concentrations in the range from 0.025 to 1.0 g/deciliter are plotted in FIG. 8 for comparison with the copolymers prepared in water and tested in water. The K value of 157.7 obtained for C=1.0 d/gL is substantially higher than the K of 141.8 obtained with the H₂O/H₂O copolymer, and this advantage persists over most of the concentration range, even compared to the samples made in water and tested in solutions of various electrolytes. (The notation H₂O/H₂O means the copolymer was prepared in water and its viscosity was determined in water.) The K values of about 178 for C=0.05 and 0.025 are inconsistent with this trend, and may represent the limit of errors in weighing or other measurements.

FIG. 9 shows plots of K values versus concentration from FIG. 8 for a limited range of concentrations equal to 0.025 to 0.1 grams/deciliter. Several of the samples prepared in water displayed an apparent maximum K value at a concentration of 0.05 g/dL. Samples of copolymers of the same 50-50 composition were then prepared in various aqueous polymerization media containing electrolytes, tested for relative viscosity at concentrations of 0.05 g/dL, and the K values calculated. As seen in FIG. 9 and Table XII, the K values for these copolymers were substantially higher than for the samples made in water. A smaller amount of variation was observed depending on the solution medium in which the polymers were tested. Maximum values were obtained for the sample prepared and tested in synthetic sea water, giving a K value of 200.4. A second polymer sample of the same composition (SSW II) prepared and tested in synthetic sea water gave a K value of 194.3. The average of these K values, 197.4, is comparable to the values obtained for other samples prepared in synthetic sea water and tested in various electrolyte solutions, and is substantially higher than the values obtained for the polymers prepared and tested in other electrolyte solutions. Tested in water, this material produced a K value of about 196. Samples prepared in saline solution produced a K value of about 192, regardless of the test medium. Samples prepared in a polymerization medium containing a mixture of NaCl and MgCl₂ produced K values ranging from 183 to 192, with the maximum being obtained for the samples tested in a solution of H₂O. While not all the differences in K values for samples prepared and tested in various media can be explained, and some differences may be due to statistical variations and/or operator error, the copolymers prepared in electrolytes, particularly synthetic sea water, NaCl or a mixture of salts, produced significantly higher K values than those copolymer samples prepared in H₂O. These polymers were of significantly higher K value than many commercial polymers, including polyvinylpyrrolidone and the polymers claimed in U.S. Pat. No. 3,500,925. Thus, while the inventive copolymers prepared in synthetic sea water or mixed electrolyte solutions are superior as reflected by their relative viscosities and K values, the copolymers prepared in H₂O or other electrolyte solutions are sufficiently viscous to be useful in certain process embodiments of the invention.

TABLE X

Calculated K values for VP-Am copolymer (50:50 wt percent) prepared in distilled water with 0.5 wt percent AIBN and tested in various media			
Conc (g/dL)	Medium	η_{rel}	K Value
1.0	H ₂ O	24.3	141.8
0.5	H ₂ O	6.44	147.6
0.25	H ₂ O	3.02	157.8
0.10	H ₂ O	1.66	166.7
0.05	H ₂ O	1.31	171.4
0.025	H ₂ O	1.14	168.2
0.5	SSW	6.70	149.3
0.25	SSW	3.15	161.0
0.10	SSW	1.70	170.8
0.05	SSW	1.33	176.3
0.025	SSW	1.15	173.9
0.5	MgCl ₂	7.04	151.4
0.25	MgCl ₂	3.30	162.1
0.10	MgCl ₂	1.64	164.6
0.05	MgCl ₂	1.32	173.9
0.025	MgCl ₂	1.15	173.9
0.5	CaCl ₂	6.86	150.3
0.25	CaCl ₂	3.18	161.7
0.10	CaCl ₂	1.63	163.6
0.05	CaCl ₂	1.32	173.9
0.025	CaCl ₂	1.14	168.2
0.5	NaCl	6.94	150.8
0.25	NaCl	3.21	162.4
0.10	NaCl	1.73	173.8
0.05	NaCl	1.30	168.8
0.025	NaCl	1.16	179.5

TABLE XI

Calculated K values for VP-Am copolymer (50:50 wt percent) prepared in SSW with 0.5 wt percent AIBN and tested in SSW		
Conc. (g/dl)	η_{rel}	K value
1.0	46.34	157.7
0.5	8.24	158.0
0.25	3.63	171.2
0.10	1.81	181.1
0.05	1.34	178.7
0.025	1.16	178.2

TABLE XII

Calculated K values for VP-Am copolymers (50:50 composition) prepared in various media with 0.5 wt percent AIBN and tested in various media. (All concentrations 0.05 g/dl)			
Polymerization Medium	Test Medium	η_{rel}	K Value
SSW	SSW	1.44	200.4
SSW/II	SSW/II	1.41	194.3
SSW	NaCl	1.43	198.4
SSW	CaCl ₂	1.43	198.4
SSW	MgCl ₂	1.43	198.4
SSW	H ₂ O	1.42	196.4
NaCl	SSW	1.40	192.2
NaCl	NaCl	1.40	192.2
NaCl	CaCl ₂	1.39	190.0
NaCl	MgCl ₂	1.39	190.0
NaCl	H ₂ O	1.39	190.0
NaCl/MgCl ₂	SSW	1.38 ^a	187.9
NaCl/MgCl ₂	NaCl	1.38	187.9
NaCl/MgCl ₂	H ₂ O	1.40	192.2
NaCl/MgCl ₂	CaCl ₂	1.37	183.6
NaCl/MgCl ₂	MgCl ₂	1.36	183.4
CaCl ₂	MgCl ₂	1.39	190.0
CaCl ₂	SSW	1.38	187.9
CaCl ₂	CaCl ₂	1.38	187.9
CaCl ₂	NaCl	1.38	187.9
CaCl ₂	H ₂ O	1.37	183.9
MgCl ₂	SSW	1.38	187.9
MgCl ₂	NaCl	1.38	187.9
MgCl ₂	MgCl ₂	1.38	187.9
MgCl ₂	CaCl ₂	1.38	187.9

TABLE XII-continued

Calculated K values for VP-Am copolymers (50:50 composition) prepared in various media with 0.5 wt percent AIBN and tested in various media. (All concentrations 0.05 g/dl)			
Polymerization Medium	Test Medium	η_{rel}	K Value
MgCl ₂	H ₂ O	1.38	187.9

^aAverage of two runs using separate batches

EXAMPLE IX

Screen Factor Tests

A series of 50/50 VP/Am copolymers was prepared in 0.7 I.S. SSW at 50 C. as previously described using AIBN as the initiator. Each copolymer solution was produced with a different amount of initiator, the range extending from 0.13 to 1.0 weight percent AIBN based on monomer weight. Each polymer solution was further diluted with SSW to provide solutions having from about 0.2 to 1 weight percent polymer. The screen factors for the various solutions were determined at 78 F and at 180 F by measuring the time required for passage of an aliquot of the polymer solution by gravity flow through five 100-mesh stainless steel screens at the designated temperature and dividing this time by the time required for passage of the same amount of SSW through these screens under identical conditions. This method is described by Foshee, et al, as previously cited.

The results obtained are plotted in FIG 10. The screen factors are directly related to the molecular weight of the polymer, e.g. how much AIBN was used in its preparation, and accordingly to its solution viscosity. The higher the molecular weight (higher the solution viscosity) the higher the screen factor over the range studied. Polymer molecular weight is inversely related to initiator concentration, as is known in the art. Consequently, the highest screen factor is obtained with the polymer prepared with the least amount of initiator. Screen factors at 180 F are smaller than their counterparts at 78 F, as expected. For example, a solution containing 1 weight percent copolymer (copolymer prepared with 0.13 weight percent AIBN) has a screen factor of about 32 at 78 F and about 7 at 180 F.

Screen factors are easier and faster to obtain than resistance factors and they can be used to estimate the relative magnitudes of the resistance factors at the same temperatures. A resistance factor describes a decrease in mobility of a polymer solution in comparison with the flow of the aqueous medium in which it is prepared. With chemically similar polymers, as the screen factor increases the resistance factor also increases. For example, screen factors measured for 0.5 weight percent solutions of the 50/50 VP/Am copolymers (prepared with 0.13, 0.25 and 1.0 weight percent AIBN in SSW) in SSW at 180 F are 3.3, 2.4, and 1.3, while preliminary average resistance factors for identical solutions measured in Berea cores are 12.1, 9.8 and 5.0, respectively. These values result in an average ratio and the screen factor for another copolymer in this group, one can estimate its resistance factor under the same conditions.

Detailed information relating to screen factors, resistance factors and the like are given by Jennings, R. R., Rogers, J. H. and West, T. J. "Factors Influencing Mobility by Polymer Solutions", J. Pet. Tech (March 1971), 391-401.

EXAMPLE X

Drilling Mud Additives

A series of five VP/Am 50/50 weight percent copolymers was prepared. Two of the samples were prepared in t-butyl alcohol using 1 weight percent t-BPP, based on the monomers, as the initiator. The remaining three samples were each prepared in saturated NaCl water, using AIBN as the initiator at weight percent levels, based on the monomers, of 10, 0.5 and 0.25, respectively. The samples prepared in NaCl water are comparison polymers.

The samples were tested in various drilling muds, as specified, for low and high temperature water loss properties, plastic viscosity, yield point value and gel strength.

The initial evaluation of the polymers was done in muds by adding 3.5 weight percent attapulgite clay to either 5 weight percent NaCl solution (base mud A) or saturated NaCl water (base mud B). Polymers submitted as solids were first ground and sifted into mud aliquots while they were stirred with a Hamilton Beach Multimixer to minimize lumping. Provision was made for polymers submitted as solutions by withholding the corresponding volume of water from the base mud when it was prepared. Water was added as necessary depending on the concentrations of the particular polymer samples. After the polymers were added to 280 mL aliquots of mud, the mud samples were stirred for 20 minutes with the Multimixer.

Before any tests were made, the mud samples were cooled to room temperature (about 25°C) while standing a minimum of 2 hours. Next, the samples were stirred 2 minutes with the Multimixer and tested with a Fann Model 35 VG meter to determine plastic viscosity, yield point value and gel strength. These tests, and a water loss test at room temperature, were made in accordance with API RP 13B. The mud pH values were also recorded. All tests were repeated after the muds were aged for 16 hours at 80°C in the absence of oxygen. Apparent viscosity was determined at 600 RPM with the VG meter assuming Newtonian flow.

For the high temperature tests, base mud A was treated with 12 lbs/bbl bentonite clay and a 2 lbs/bbl Desco® thinner, Phillips Petroleum Co., a blend of sulfomethylated quebracho and sodium dichromate, along with sufficient NaOH to obtain the desired pH before addition of the polymers. Polymer addition and initial testing were done at room temperature as in the low temperature tests. After the initial tests, the mud samples were aged in brass bombs in the absence of oxygen for 16 hours at 360°F. After aging, the muds were cooled to room temperature, stirred for 2 minutes with the Multimixer, and tests on plastic viscosity, yield point value, pH, and water loss were repeated. The final test on these muds was a high temperature water loss test performed at 325°F and 500 psi differential pressure.

In the Tables the polymers are identified as follows.

Polymer 1, made in t-butyl alcohol with 1 weight percent t-BPP based on the monomers.

Polymer 2, like 1, except submitted as a solid for testing.

Polymer 3, made in saturated NaCl water, 1 weight percent AIBN based on the monomers.

Polymer 4, like 3 except used 0.5 weight percent AIBN.

Polymer 5, like 3 except used 0.25 weight percent AIBN.

The results are reported in Tables XIII, XIV, and IV. The results presented in Tables XIII and XIV indicate that at low polymer concentrations, e.g. about 1 lb/bbl mud, made with 3.5 weight percent attapulgite clay in 5 weight percent NaCl water or in saturated NaCl water, relatively poor water loss performance in both unaged and in aged test samples was noted. However, when the amount of polymer was increased to about 3 or 4 lbs polymer bbl mud, water loss values for the unaged and aged samples were low, e.g. about 5-7 mL/30 minutes at room temperature.

Table XV summarizes the performance of the copolymers in hard brine muds. The hard brine was a synthetic brine prepared by dissolving 1235 g NaCl, 308 g CaCl₂ and 78.5 g MgCl₂·6H₂O in 5000 mL of tap water. The calculated calcium ion concentration in this brine is 1.68 weight percent.

The results in Part A of Table XV indicate that in mud prepared by mixing 2 lbs/bbl of asbestos fiber and 16 lbs/bbl of P95 illite clay from Roger Lake, Calif. in the hard brine, the water loss values of an inventive copolymer prepared in t-butyl alcohol were equivalent or better than those obtained with a commercially available mud additive (Driscal® II) when the polymers are used at 2 lbs/bbl under conditions employed. With lesser amounts of polymer, the commercial polymer is superior under such test conditions. (Driscal® II is a 50/50 weight percent mixture of carboxymethylhydroxyethyl cellulose and polyethylene glycol having a molecular weight of about 8,000 available from Drilling Specialties Co., Bartlesville, Okla. 74004).

The data in part B of Table XV show that inventive polymer 2 is more effective (lower water loss results) than comparison polymer 4 in the mud absent the Flo-sal® fiber (asbestos fiber) but in the presence of added bentonite clay. However, in this test the commercial polymer gave somewhat better results, e.g. lower water loss, than inventive polymer 2.

The high temperature water loss values for a mud composed of 12 lbs/bbl bentonite clay, 2 lbs/bbl Desco® thinner and sufficient NaOH to give a pH of about 10-12 admixed with base mud A (3.5 weight percent attapulgite clay in 5 weight percent NaCl water), in the presence or absence of 1 lb/bbl of gypsum, are presented in Table XVI. The water loss data show that inventive polymer 2 initially gives somewhat higher results at room temperature than those obtained with the commercial polymer Drispac® Superlo, a carboxymethyl cellulose of Drilling Specialties Co. However, after aging the polymers for 16 hours at 360°F and retesting them at room temperature, the data show the inventive polymer to be clearly superior to Superlo in the absence or presence of added gypsum. The water loss data also show the inventive polymer to perform better in the absence of gypsum, both initially and after aging, than the commercial polymer, Cypan® sodium polyacrylate of American Cyanamide. However, aged Cypan performs somewhat better than the aged invention copolymer in mud containing gypsum.

The water loss data additionally show the comparison polymers to be equivalent or better in performance than inventive polymer 2 in initial testing and especially after aging the polymers, both in the absence or presence of gypsum. Very low high temperature water loss results are also obtained with the comparison polymer. Based on superior results presented before with the

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inventive polymers prepared in SSW, whether aged or unaged, relative to those made in NaCl or other aqueous solution containing one or two electrolytes, it is

believed that said inventive polymers will outperform the comparison polymers in drilling mud applications as well

TABLE XIII

Screening Tests in Base Mud A										
Polymer Conc lb/bbl	Initial Properties					Aged 16 Hours at 80 C.				
	AV*	PV/YP**	Gels**	pH	WL**	AV	PV/YP	Gels	pH	WL*
Base Mud***	5.5	2/7	7/9	8.2	173	6	3/6	5/6	8.2	174
<u>Polymer 1</u>										
1	11	6/10	4/8	8.0	26	16	7/18	8/14	8.3	100
3	12	10/4	2/3	8.0	7.5	13	10/6	0/0	8.3	9.1
<u>Polymer 3</u>										
1	10.5	8/5	3/5	8.1	42	10	7/6	4/5	8.2	159
<u>Polymer 5</u>										
1	16	9/14	7/7	8.2	50	17.5	8/19	7/7	8.1	138

*Apparent viscosity cP (assuming Newtonian flow and a shear rate of 1022 reciprocal seconds).

**PV — Plastic viscosity, cp

YP — Yield point, lb/100 sq. ft.

Gels — Gel strength, 10 sec/10 min., lb/100 sq. ft.

WL — API water loss, mL/30 minutes

***Base Mud A — 3.5 percent attapulgite clay in 5 percent NaCl solution.

TABLE XIV

Screening Tests in Base Mud B										
Polymer Conc. lb/bbl	Initial Properties					Aged 16 Hours at 80 C.				
	AV*	PV/YP	Gels	pH	WL***	AV	PV/YP	Gels	pH	WL***
Base Mud**	8	4/8	6/9	7.7	138	9.3	4/9	5/5	7.7	129
<u>Polymer 1</u>										
1	12.5	8/9	6/8	7.6	75	—	—	—	—	—
3	16.5	14/5	1/1	7.8	5.4	—	—	—	—	—
<u>Polymer 2</u>										
1	21.5	10/23	11/15	7.8	105	—	—	—	—	—
3	23	17/12	2/3	7.5	6.8	27	20/14	1/2	7.9	5.5
<u>Polymer 3</u>										
1.00	14	10/8	5/5	7.6	56	14.5	10/9	6/6	7.6	146
1.25	15	12/6	2/4	7.3	21	12.5	8/7	3/4	7.8	85
3.75	43.5	30/27	3/4	7.3	5.6	35	31/8	2/2	7.8	6.3
<u>Polymer 4</u>										
1.25	15	11/8	3/4	7.4	16	13.5	9/9	4/6	7.9	64
3.75	44.5	31/27	3/3	7.4	5.7	35.5	28/15	2/2	7.7	5.5
<u>Polymer 5</u>										
1	13.5	9/9	4/6	7.6	47	13	8/10	6/7	7.6	190
1.25	14	12/4	1/3	7.4	18.5	12.5	9/7	3/4	7.6	111
3.75	46	32/28	2/3	7.4	5.5	37.5	28/19	2/2	7.7	5.0

*AV — Apparent viscosity cP (assuming Newtonian flow and a shear rate of 1022 reciprocal seconds).

**Base Mud B — 3.5 percent attapulgite clay in saturated NaCl water

***Water loss, mL/30 minutes

TABLE XV

Screening Tests in Hard Brine* Muds							
Materials Conc., lb/bbl			Initial Properties		Aged 16 Hours at 80 C		
			PV/YP	Gels	WL	PV/YP	Gels
AM/VP	Driscoll # II		(pH 6.4-7.0)			(pH 6.1-6.4)	
Part A Muds Prepared with 2 lb/bbl Flocal # fiber and 16 lb/bbl P95 White clay from Rogers Lake, California							
—	—		6/15	18/14	180	—	—
—	1		8/10	14/10	14.5	6/9	5/3
—	2		12/22	29/20	7.9	11/19	3/3
Polymer 2							
1	—		7/16	19/15	23.0	8/18	11/12
2	—		10/7	14/10	7.0	7/10	5/7
Part B Muds Prepared without Flocal fiber but treated with 16 lb/bbl P95 clay and other clays as specified (16 lb/bbl bentonite clay added)							
—	—		3/1	1/2	95	—	—
—	1		4/6	1/10	25	—	—
Polymer 2			3/1	1/1	57	—	—
1			10 lb/bbl bentonite clay added				
Polymer 4			4/1	1/1	82**	—	—
1							

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TABLE XV-continued

<u>Screening Tests in Hard Brine^a Mud</u>							
<u>Initial Properties</u>				<u>Aged 16 Hours at 80 C</u>			
<u>Materials Conc., lb/bbl</u>		<u>FV/YP</u>	<u>Gels</u>	<u>WL</u>	<u>FV/YP</u>	<u>Gels</u>	<u>WL</u>
<u>AM/VP</u>	<u>Drusac ® II</u>	<u>(pH 6.4-7.0)</u>			<u>(pH 6.1-6.4)</u>		
<u>No additional clay added</u>							
<u>Polymer 4</u>							
—	1	6/2	1/1	14.8	—	—	—
3	3	4/1	1/1	21.0	—	—	—
1	—	5/0	0/1	98.9 ^b	—	—	—
1	—	4/1	1/1	137 ^b	—	—	—
<u>The above test was repeated with the opposite order of addition</u>							
1	—	4/1	1/1	82 ^b	—	—	—

^aHard Brine-Synthetic brine prepared by adding 1235 g NaCl, 308 g CaCl₂, and 78.5 g MgCl₂·6H₂O to 5000 ml tap water. The calcium ion concentration is calculated to be 1.675 percent by weight.

^bThese WL values were calculated after a one minute test.

TABLE XVI

High Temperature Tests - Effect of Gypsum										
Materials Conc., lb/bbl		Initial Properties				Aged 16 Hours at 360 F				
Polymer	Gypsum	FV/YP	Gels	pH	WL	FV/YP	Gels	pH	WL	HTWL
Base Mud ^a										
—	—	3/4	5/11	10.0	86	3/6	10/31	7.9	137	—
—	1	3/3	4/10	9.7	100	3/4	5/14	7.8	130	—
Part A Commercial Drilling Mud Additives										
Drusac ® Superio										
3	—	31/20	2/6	9.3	6.0	5/5	5/13	7.0	90	—
3	1	27/15	2/5	9.2	5.0	3/5	5/10	7.6	110	—
Cypac ® sodium polyacrylate										
3	—	6/2	2/5	11.6	14.0	4/2	0/1	8.7	54	—
3	1	5/3	2/6	11.6	17.3	2/4	1/1	8.7	37	74
Part B Experimental VF/Am Copolymers										
Polymer 2										
3	—	18/22	7/11	9.3	9.2	17/42	12/12	7/3	17.0	—
3	1	17/22	7/12	9.8	10.0	14/46	14/16	7.3	64.0	—
Polymer 3										
2	—	14/10	3/6	11.7	8.9	16/14	2/3	9.1	8.4	54
2	1	15/7	2/6	11/6	10.4	17/14	2/3	9.1	8.6	36
1.75	—	26/34	4/10	11.5	5.5	31/44	6/7	8.5	6.0	23
1.75	—	26/29	3/9	11.2	5.7	29/40	6/8	8.2	6.0	27
Polymer 4										
1.75	—	29/33	4.8	11.4	5.7	30/44	5/6	8.5	5.8	28
1.75	1	27/31	4/9	11.3	5.8	28/41	7/8	8.2	5.5	29
Polymer 5										
2	—	16/10	2/6	11.7	8.4	16/12	2/3	9.0	9.6	50
2	1	14/10	3/6	11.6	9.7	13/12	2/3	9.0	9.3	48
1.75	—	27/37	4/8	11.5	5.9	30/48	6/7	8.4	6.0	24
1.75	1	28/36	4/7	11.4	6.3	25/40	6/6	8.3	6.1	26

^aThe mud for these tests was prepared by adding 12 lb/bbl bentonite clay, 2 lb/bbl Drusac ® thinner and NaOH to Base Mud A, Base Mud A is 1.5% amorphous clay in 5 percent NaCl water.

^bHTWL — High temperature, high pressure water loss, API, mL/30 min. at 315° F and 300 psi.

EXAMPLE XI

Preparation and Properties of PVP Homopolymer

This example describes the preparation and the aqueous solution viscosity behavior of poly(N-vinyl-2-pyrrolidone). This homopolymer sample of N-vinyl-2-pyrrolidone was prepared in accordance with the inventive polymerization procedure described previously herein, i.e., polymerization of N-vinyl-2-pyrrolidone (VP) in synthetic seawater (0.7 ionic strength) initiated by azobisisobutyronitrile (AIBN).

A charge of 20.0 g N-vinyl-2-pyrrolidone was placed in a 10-ounce crown top polymerization bottle with 0.10 g azobisisobutyronitrile (AIBN) initiator and a 200 g portion of synthetic seawater. The initiator level was 0.5 wt. % AIBN, based on the weight of monomers charged. A stock solution of the synthetic sea water was prepared by dissolving the approximate amounts of the

specified electrolytes in sufficient deionized water to prepare 18 liters of solution.

Electrolyte	Approximate Wt. Electrolyte (g)	Approximate Electrolyte Concentration (g/liter)
NaHCO ₃	3.7	0.2
Na ₂ SO ₄	77.2	4.3
NaCl	429	23.8
CaCl ₂ ·2H ₂ O	29.6	1.6
MgCl ₂ ·6H ₂ O	193.9	10.8

The ionic strength of the synthetic seawater was about 0.7. The reaction mixture was degassed for 20 minutes before the polymerization vessel was placed in a 50° C. constant temperature water bath. The polymerization reaction vessel was secured in a rack and rotated continuously for 25 hours at 50° C. At the end of the reaction

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period, the reaction mass was homogeneous and mobile, and very viscous.

A suitable experimental sample for viscosity measurements was prepared by combining a 100 g portion of the polymerization reaction mass with 400 g of synthetic seawater. This dilution gave a mixture which was about 1.8 wt. percent polymer. Before combining the polymer sample with the synthetic seawater, the latter was purged with N₂ in a dry box for 2 hours. The oxygen content of the synthetic seawater after the N₂ purge was about 5 ppb (parts per billion). After mixing the polymer sample and synthetic sea water, the solution was further purged with N₂ for 3 hours in a dry box before any solution viscosities were determined. A similar solution of a commercially available poly(N-vinyl-2-pyrrolidone) (GAF PVP K-100) was also prepared for viscosity measurements for comparison.

The respective solutions of experimental and commercial poly(N-vinyl-2-pyrrolidone) polymers were aged at 200 F and 250 F to determine the effect of thermal aging on solution viscosities. After a specified aging period, individual sample solutions were cooled to ambient temperature before measuring Brookfield viscosity at the designated rpm. Results are summarized in Table XVII. The initial viscosity of the experimental solution was 16.1 cp at 6 rpm, whereas the initial viscosity of the commercial polymer solution was about 13.1 cp at 5 rpm.

TABLE XVII

Viscosities of PVP* Solutions After Thermal Aging						
Type of Run	Aging Period (Days) @200 F	Viscosity (cP)	% Initial Viscosity Lost (200 F)	Aging Period (Days) @250 F	Viscosity (cP)	% Initial Viscosity Lost (250 F)
Control	0	13.1	0.0	0	13.1	0.0
(Commercial K-100 PVP)	6	10.4	20.6	6	9.2	29.8
	19	9.2	29.8	19	11.8	9.9
	41	7.9	39.7	40	10.5	19.8
	118	9.2	29.8	118	9.2	29.8
Invention (Experimental PVP)	0	16.1	0.0	0	16.1	0.0
	21	14.2	11.8	21	13.8	14.3
	48	14.0	13.0	48	13.6	15.5
	95	13.5	16.1	95	13.2	18.0
	139	13.8	14.3	129	13.5	16.1
	245	13.7	14.9	245	13.6	15.5

*PVP represents poly(N-vinyl-2-pyrrolidone).

Referring to the results in Table XVII, it is evident that the initial viscosity of the experimental polymer solution was not only higher than that of the control run (16.1 centipoise vs. 13.1 centipoise) but on thermal aging at either 200 F or 250 F., the experimental polymer solution exhibited a lower percentage loss of the initially observed solution viscosity than did the commercially available polymer solution. See FIG 11, in which the viscosities of these samples are plotted versus aging time. It is noteworthy that the control system solution viscosity aged at either 20 F or at 250 F had diminished by about 30 percent of the initial viscosity in a time period of 118 days, whereas the solution viscosity of the experimental system even on aging for 245 days at either 200 F or at 250 F had diminished by only about 15 percent of the initial viscosity.

EXAMPLE XII

PVP Viscosities

N-Vinyl-2-pyrrolidone was polymerized in synthetic seawater at three initiator levels of AIBN in a procedure essentially the same as described in Example XI. A control run was carried out involving the polymeriza-

tion of N-vinyl-2-pyrrolidone in distilled water. Samples of the poly(N-vinyl-2-pyrrolidone) polymers as 2 wt. percent solutions in synthetic sea water were used in Brookfield viscosity determinations and the results are summarized in Table XVIII.

TABLE XVIII

Solution Viscosities of PVP Samples				
Run No.	AIBN Initiator Level (wt. %)	Type of Run	Viscosity (cP)	Polymerization Medium
1	1.0	Control	9.0	Distilled H ₂ O
2	1.0	Invention	18.5	SSW*
3	0.5	Invention	23.4	SSW*
4	0.25	Invention	25.8	SSW*

*The preparation of the synthetic sea water is given in Example XI.

Referring to the results in Table XVII (see runs 1 and 2), it is evident that the solution viscosity of the poly(N-vinyl-2-pyrrolidone) prepared in synthetic seawater with 1.0 percent AIBN initiator was approximately twice that observed for the PVP similarly prepared in distilled water. Runs 3 and 4 illustrate that greater solution viscosities for the inventive poly(N-vinyl-2-pyrrolidone) samples resulted on the use of lower levels of AIBN initiator, presumably because of the higher molecular weights obtained in runs 3 and 4 relative to the molecular weight obtained in run 1. (This effect has been noted previously in other examples and in the detailed description.)

EXAMPLE XIII

In Situ Polymerization for Permeability Correction

This example describes the in situ copolymerization of N-vinyl-2-pyrrolidone and acrylamide to effect a permeability correction in a high salinity, high temperature oil-bearing subterranean formation. Suitable ratios of monomers, for example, N-vinyl-2-pyrrolidone and acrylamide, vary over the broad range as disclosed earlier herein. In the following calculated example, the weight ratio of N-vinyl-2-pyrrolidone (VP) to acrylamide (Am) is 60.40, which corresponds to about 1 mole of VP to 1 mole of Am.

CALCULATED EXAMPLE

Two pore volumes (based upon the intended area of treatment) of a one weight percent aqueous solution of sodium-1-naphthylamine-4-sulfonate polymerization inhibitor is introduced through an injection well into an exhaustively waterflooded, oil-bearing subterranean formation with a reservoir temperature in the range of

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about 250 F and a connate water salinity on the order of 200,000 ppm total dissolved solids containing up to 60,000 ppm or higher of divalent cations such as Ca++ and Mg++ Said formation has been subjected to secondary waterflooding prior to injection of the polymerization inhibitor to such an extent that the injected water is channeling through the high permeability zones and the water to oil ratio out the producing wells is very high, e.g. greater than about 100:1

After all of the polymerization inhibitor slug has been introduced, a 0.5 pore volume slug of predominantly aqueous sodium chloride containing about 15000 ppm total dissolved solids is used to flush the previously injected polymerization inhibitor from the more permeable zones without completely removing same from the less permeable zones

An in situ copolymerization treatment slug comprising about 90 weight percent saline water based on total weight of the slug, admixed with an equimolar mixture of N-vinyl-2-pyrrolidone (VP) and acrylamide (Am) (60 parts by weight VP and 40 parts by weight Am), and 0.5 weight percent AIBN (azobisisobutyronitrile or other suitable initiator, based on total weight of monomers) is injected following the flushing of the polymerization inhibitor from the high permeability zones. The saline water used in preparing the in situ copolymerization treatment slug can be any available water compatible with the formation, but is preferably characterized by an ionic strength of about 0.7 and contains a mixture of electrolytes such as, e.g., NaHCO₃, NaCl, CaCl₂, Na₂SO₄, and MgCl₂ The in situ copolymerization is allowed to progress undisturbed for a period of approximately 24 hours.

At the end of 24 hours, a tertiary oil recovery surfactant flood is carried out, e.g., in a manner as described in U.S. Pat. No. 4,343,711 Oil recovery is increased as evidenced by a lower water to oil ratio at the producing wells

EXAMPLE XIV

Preparation of Terpolymers

As previously disclosed, this invention encompasses terpolymer compositions. Specific terpolymers prepared and tested can be described by the formula



wherein VP represents N-vinyl-2-pyrrolidone derived units as an N-vinyl lactam, Am represents acrylamide derived units as an unsaturated amide, and monomer X represents units derived from various monomers such as methyl methacrylate (MMA), methyl acrylate (MA), butyl acrylate (BA), hydroxyethyl acrylate (HEA), lauryl methacrylate (LMA), acrylonitrile (AN), vinyl acetate (VA), styrene (STY), 4-vinyl pyridine (4-VPy), 5-methyl-2-vinylpyridine (MVPy), and mixtures thereof. The chemically-initiated preparations of representative terpolymers in various polymerization media are described hereinafter.

(A) Deionized Water Polymerization Medium (Control)

A charge of 27.9 g N-vinyl-2-pyrrolidone (VP), 27.9 g acrylamide (Am) and 4.2 g methyl methacrylate (MMA) was placed in a one quart crown top beverage bottle together with 600 g deionized water and 0.08 g azobisisobutyronitrile initiator (AIBN, 0.13 wt percent based on total weight of charged monomers). Reaction

mixtures were routinely degassed for 20 to 30 minutes before sealing. The charged bottle was rotated for about 16 hours in a constant temperature bath at 50° C. On removing the bottle from the bath and cooling to room temperature, the instant product mixture appeared to be a viscous fluid somewhat cloudy and whitish in color. This procedure yielded a 46.5:46.5:7.0 weight percent VP/Am/MMA terpolymer.

Table XIX (below) discloses a variety of VP/Am/MMA terpolymers prepared in deionized water.

TABLE XIX

Deionized Water Polymerization Medium			
Run	Wt % VP	Wt % Am	Wt % MMA
1	ca. 49.88	ca. 49.88	0.25
2	49.75	49.75	0.50
3	49.5	49.5	1.00
4	49.0	49.0	3.00
5	48.5	48.5	3.00
6	47.5	47.5	5.00
7	46.5	46.5	7.00
8	45.0	45.0	10.00

*Initiator was 0.13 wt. percent AIBN based on total monomers charged.

(B) Synthetic Sea Water Polymerization Medium (Invention)

The preparative procedure was essentially the same as that described in (A) except for the use of synthetic seawater (SSW) as the polymerization medium. The composition and preparation of the synthetic seawater is described hereinafter.

For example, the following charge was placed in a 10 oz. crown top reactor bottle to prepare a 48.5:48.5:3.0 weight percent VP/Am/MMA terpolymer.

9.7 g	N-vinyl-2-pyrrolidone (VP)
9.7 g	Acrylamide (Am)
0.6 g	Methyl Methacrylate (MMA)
0.025 g	Azobisisobutyronitrile (AIBN, 0.125 wt. percent)
200 g	Synthetic Seawater (SSW)

Table XX (below) discloses a variety of VP/Am/MMA terpolymers prepared in synthetic seawater.

TABLE XX

Synthetic Seawater Polymerization Medium (0.7 ionic strength)				
Run No.	Wt % VP	Wt % Am	Wt % MMA	Wt % AIBN*
9	49.5	49.5	1.0	0.125
10	47.5	47.5	5.0	0.125
11	49.5	49.5	1.0	0.250
12	48.5	48.5	3.0	0.250
13	48.0	48.0	4.0	0.250
14	47.5	47.5	5.0	0.250
15	47.0	47.0	6.0	0.50
16	49.5	49.5	1.0	0.50
17	48.5	48.5	3.0	0.50
18	48.0	48.0	4.0	0.50
19	47.5	47.5	5.0	0.50
20	47.0	47.0	6.0	0.50

*Azobisisobutyronitrile initiator (AIBN, wt percent based on total monomers charged).

(C) Sodium Chloride Solution Polymerization Medium (Control) (0.7 ionic strength)

The preparative procedure was essentially the same as that described in (A) except for the use of aqueous sodium chloride solution as the polymerization medium. The 1.5 liter batches of 0.7 ionic strength salt stock

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solution were prepared by dissolving 61.36 g NaCl in 1440 mL of deionized water

For example, the following charge was placed in a one quart crown top reactor bottle to prepare a 48.5:48.5:3.0 weight percent VP/Am/MMA terpolymer

29.1 g	Acrylamide (Am)
1.5 g	Methyl Methacrylate (MMA)
0.08 g	Ascorbic acid (AIBN)
	0.130 wt. percent
600 g	Sodium Chloride Solution (0.7 ionic strength)

Table XXI (below) discloses a variety of VP/Am/MMA terpolymers prepared in 0.7 ionic strength aqueous sodium chloride solution

Table XXII (below) discloses additional terpolymers prepared in 0.7 ionic strength aqueous sodium chloride solution.

TABLE XXI

Aqueous NaCl Polymerization Medium (0.7 ionic strength)			
Run ^{a,b}	Wt % VP	Wt % Am	Wt % MMA
21	ca. 49.88	ca. 49.88	0.25
22	49.75	49.75	0.30
23	49.5	49.5	1.00
24	49.0	49.0	2.00
25	48.5	48.5	3.00
26	47.5	47.5	5.00
27	46.5	46.5	7.00
28	45.0	45.0	10.00
29	49.5	49.5	1.00

^aInitiator was 0.13 wt. percent AIBN based on total monomers charged (Runs 21-28).

^bInitiator was 0.125 wt percent AIBN based on total monomers charged (Run 29).

TABLE XXII

Terpolymers Prepared in Aqueous NaCl Solution (0.7 ionic strength)			
Run	Wt % VP	Wt % Am	Termonomers ^{a,c}
41	49.5	49.5	Methyl Acrylate (MA)
42	49.5	49.5	Butyl Acrylate (BA)
43	49.5	49.5	Hydroxyethyl Acrylate (HEA)
44	49.5	49.5	Lauryl Methacrylate (LMA)
45	49.5	49.5	Acrylonitrile (AN)
46	49.5	49.5	Vinyl Acetate (VA)
47	49.5	49.5	Styrene (STY)
48	49.5	49.5	4-Vinyl Pyridine (4-VPy)
49	49.5	49.5	5-Methyl-2-Vinyl Pyridine (5-MVPy)
50	49.5	49.5	Mixture (MMA + VA) ^d

^aThe termonomer was present in 1.00 wt percent based on total weight of monomers charged.

^b0.5 wt. percent methyl methacrylate + 0.5 wt percent vinyl acetate based on total weight of monomers charged

^c0.130 wt. percent AIBN initiator

(D) Tertiary-Butyl Alcohol Polymerization Medium (Invention)

the preparative procedure was essentially the same as that described in (A) except for the use of tert-butyl alcohol as the polymerization medium and the use of tert-butyl peroxyisobutyrate as the initiator. Terpolymer products were precipitated by dilution of the reaction mixture with hexane and removed by suction filtration

In a typical run, e.g., the following charge was placed in a 10 oz crown top reactor bottle to prepare a 47.5:47.5:5.0 weight percent VP/Am/MMA terpolymer

9.5 g	N-vinyl 2-pyrrolidone (VP)
9.5 g	Acrylamide (Am)
1.0 g	Methyl Methacrylate (MMA)
0.025 g	Tert-butyl peroxyisobutyrate (0.125 wt percent)
200 mL	Tert-butyl alcohol

At the end of a 27 hour reaction period, the reaction mixture was poured into stirring hexane to precipitate the terpolymer product. The product was isolated by suction filtration and dried in vacuo (20.45 g, ca. quantitative)

Tables XXIII and XXIV (below) disclose a variety of VP/Am/MMA terpolymers prepared in tert-butyl alcohol

TABLE XXIII

Tertiary Butyl Alcohol Polymerization Medium				
Run No	Wt % VP	Wt % Am	Wt % MMA	Wt % I ^a
30	47.5	47.5	5.0	0.125
31	45.0	45.0	10.0	0.125
32	47.5	47.5	5.0	0.250
33	45.0	45.0	10.0	0.250
34	47.5	47.5	5.0	0.50
35	45.0	45.0	10.0	0.50
36	65.0	30.0	5.0	0.50
37	65.0	25.0	10.0	0.50
38	47.5	47.5	5.0	0.50
39	30.0	65.0	5.0	0.50
40	25.0	65.0	10.0	0.50

^aInitiator was t-butyl peroxyisobutyrate (Wt percent based on total weight of charged monomers).

TABLE XXIV

Terpolymerization ^a Using Styrene, Vinyl Acetate And Lauryl Methacrylate Termonomers				
Run No.	Wt % VP	Wt % Am	Termonomers ^{a,c,d}	Wt % I ^a
51	65.0	30.0	5.0	0.30
52	65.0	20.0	10.0	0.50
53	30.0	65.0	5.0	0.50
54	25.0	65.0	10.0	0.50
55	47.5	47.5	5.0	0.50
56	45.0	45.0	10.0	0.50
57	47.5	47.5	5.0	0.25
58	45.0	45.0	10.0	0.25
59	47.5	47.5	5.0	0.25
60	47.5	47.5	5.0	0.125
61	48.75	48.75	2.5	0.50

^aTert-butyl alcohol was the polymerization medium.

^bTermonomer was vinyl acetate (Runs 51-58).

^cTermonomer was styrene (Runs 59, 60).

^dTermonomer was lauryl methacrylate (Runs 61-64).

^e0.1 wt. percent t-butyl peroxyisobutyrate initiator (based on total monomers)

The following examples demonstrate the thermal stability of various terpolymer compositions (see Example XIV) in synthetic seawater at elevated temperatures. Solution Brookfield viscosities were measured in the thermal aging tests and retention of solution viscosity was taken as a manifestation of terpolymer stability under the test conditions. Selected data are tabulated hereinbelow

EXAMPLE XV

Thermal Aging of Terpolymers

Test samples, e.g., of VP/Am/MMA terpolymer solutions were prepared by combining sufficient terpolymer with synthetic seawater (SSW, 0.7 ionic strength) to give a 0.5 wt percent (5000 ppm) solution of the terpolymer (active basis). The test solution was

purged of oxygen by inert gas entrainment before running the thermal aging tests. Aging tests were routinely carried out by incubating sealed samples at 200 F, 250 F and 300 F for specified time periods. After cooling the samples, Brookfield viscosities of the thermally aged samples were determined at 77 F to determine viscosity retention of the solution after subjection to elevated temperatures in the presence of electrolytes. The results are shown in Table XXV.

All of the tests shown in Table XXV involved the use of terpolymers prepared in synthetic seawater with an initiator level of 0.5 wt percent AIBN (based on total monomers).

TABLE XXV

Aging Period (Days)	200 F Aging Viscosity (cP)	250 F Aging Viscosity (cP)	300 F Aging Viscosity (cP)
Thermal Aging of 47.5/47.5/3.0 Weight Percent VP/Am/MMA Terpolymer			
0 days	7.5	7.5	7.5
23 days	9.9	8.7	8.5
56 days	9.7	7.7	5.6
112 days	9.4	8.0	6.4
190 days	9.3	8.3	4.5
Thermal Aging of 48.5/48.5/3.0 Weight Percent VP/Am/MMA Terpolymer			
0 days	9.0	9.0	9.0
12 days	11.7	11.4	7.1
43 days	12.5	11.0	5.1
68 days	11.4	10.3	7.0
118 days	12.4	10.2	7.5
Thermal Aging of 49.5/49.5/1.00 Weight Percent VP/Am/MMA Terpolymer			
0 days	10.3	10.3	10.3
17 days	14.1	12.6	7.1
57 days	14.2	12.6	6.2
83 days	14.0	12.0	7.9
133 days	13.9	12.4	8.1

Referring to the results in Table XV, it is evident that good retention of solution viscosity was noted in all three terpolymer compositions after aging at 200 F and 250 F. Attention is called to the fact that the terpolymers containing 1 wt percent and 3 wt percent methyl methacrylate (MMA) retained a greater percentage of the initial solution viscosity in the 300 F tests than did the terpolymer containing 5 wt percent MMA, viz., 79 percent viscosity retention and about 83 percent viscosity retention compared to 60 percent viscosity retention.

EXAMPLE XVI

Thermal Aging of Terpolymers

All of the tests shown in Table XXVI involved the use of terpolymers prepared in synthetic seawater with an initiator level of 0.125 wt. percent AIBN (based on total monomers). Test samples were 0.5 weight percent terpolymer in synthetic seawater for viscosity measurements taken at 77 F after aging at the indicated elevated temperature.

TABLE XXVI

Aging Period (Days)	200 F Aging Viscosity (cP)	250 F Aging Viscosity (cP)	300 F Aging Viscosity (cP)
Thermal Aging of 47.5/47.5/3.0 Weight Percent VP/Am/MMA Terpolymer			
0	12.1	12.1	12.1
13	13.6	15.6	12.0
41	17.1	11.3	6.5
101	16.9	13.5	6.7
147	9.7	13.3	7.7

TABLE XXVI-continued

Aging Period (Days)	200 F Aging Viscosity (cP)	250 F Aging Viscosity (cP)	300 F Aging Viscosity (cP)
Thermal Aging of 48.5/48.5/3.0 Weight Percent VP/Am/MMA Terpolymer			
0	13.8	13.8	13.8
18	17.6	16.7	9.9
46	19.6	16.3	9.0
105	19.6	15.1	9.3
148	19.0	15.8	8.2
Thermal Aging of 49.5/49.5/1.00 weight percent VP/Am/MMA Terpolymer			
0	14.2	14.2	14.2
13	20.0	17.5	4.6
47	17.3	17.5	12.4
106	21.2	18.5	7.8
149	16.5	14.4	10.2

Referring to the results in Table XXVI, it is evident that the initial solution viscosity values for the three terpolymers (12.1, 13.8, 14.2) are significantly greater than the corresponding values in Table XXV (7.5, 9.0, 10.3). Presumably, this is due to the higher average molecular weights of the Table XXVI terpolymers, which can be attributed to lower levels of initiator, viz., 0.125 wt percent AIBN compared to 0.50 wt. percent AIBN. It is evident that the solution sample containing 1 wt. percent methyl methacrylate terpolymer retained a greater percentage of the initial solution viscosity in the 300 F tests than did the terpolymers containing 3 wt percent and 5 wt. percent MMA, viz., about 72 percent viscosity retention compared to about 59 percent viscosity retention and about 65 percent viscosity retention. The viscosity of 9.7 obtained upon aging the 5 wt. percent MMA terpolymer for 147 days at 200 F appears lower than would be expected, probably due to the presence of oxygen or other operator error.

In general, it is believed that the apparent fluctuations of solution viscosities noted throughout the thermal aging tests are related to the extent of the percent hydrolysis of pendant $-\text{CONH}_2$ groups, since it is well known that the viscosifying effectiveness of polyacrylamides passes through a maximum as a function of the degree of hydrolysis of amide moieties along the polymer backbone. The variously structured terpolymers could well vary in their inherent tendency to undergo hydrolysis of pendant amide groups along the polymer backbone.

EXAMPLE XVII

Terpolymer Cloud Point Temperatures

This example discloses cloud point determinations of terpolymer compositions prepared as hereinbefore described in Examples XV and XVI which had been aged in synthetic seawater at temperatures in the range of 200-300 F. Results are summarized in Table XVII.

TABLE XXVII

Cloud Point Determinations on VP/Am/MMA Terpolymer Prepared in Synthetic Seawater			
Thermal Aging Days @ F	Cloud Points F (After Aging)		
	1% MMA	3% MMA	5% MMA
157 @ 300 F*			275.6
160 @ 300 F	300.7	289	
182 @ 300 F	297.6		282.0
186 @ 300 F		293.6	
202 @ 300 F	>298		
214 @ 300 F		295.6	
181 @ 250 F	254.4		
186 @ 250 F		239.0	

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TABLE XXVII-continued

Cloud Point Determinations on VP/Am/MMA Terpolymer Prepared in Synthetic Seawater			
Thermal Aging Days @ F	Cloud Points °F (After Aging)		
	1% MMA	3% MMA	5% MMA
202 @ 250 F	255.8		
214 @ 250 F		239.8	
181 @ 200 F ^a	253.5		
202 @ 200 F	282.1		
51 @ 300 F ^b			243.5
66 @ 300 F		262.2	
76 @ 300 F			258.6
79 @ 300 F	285.6		
84 @ 300 F	273.5		
98 @ 300 F	288.8		
113 @ 300 F	289.3		
113 @ 250 F ^b	255.9		
112 @ 200 F ^b	>300		

^aAzobisisobutyronitrile initiator level was 0.125 wt. percent
^bAzobisisobutyronitrile initiator level was 0.5 wt. percent

Referring to the results in Table XXVII, it is evident that the terpolymers containing 1 wt percent MMA and 3 wt. percent MMA exhibit somewhat higher cloud points under comparable conditions than terpolymers containing 5 wt. percent MMA. This observation was apparent for terpolymerization initiated by 0.125 wt. percent AIBN or 0.50 wt percent AIBN.

EXAMPLE XXVIII

Stability of Thermally Aged Terpolymers

This example demonstrates the thermal stability of terpolymer compositions containing varying amounts of methyl methacrylate (MMA), the balance being equal weights of acrylamide (Am) and N-vinyl-2-pyrrolidone (VP). Solution viscosities were determined at different temperatures by capillary viscometry as is well known in the art. In general, 0.25 weight percent solutions of the terpolymers were aged at 300 F for seven days before viscosities were determined. Two terpolymers were studied: (1) a VP/Am/MMA polymer (49.5 wt % VP, 49.5 wt % Am, 1.0 wt % MMA) prepared in synthetic seawater with an AIBN level of 0.125 wt. percent based on total monomers charged, and (2) a VP/Am/MMA terpolymer (47.5 wt % VP, 47.5 wt % Am, 5.0 wt % MMA) prepared in synthetic seawater with an AIBN level of 0.13 wt percent. Results are summarized in Table XXVIII.

TABLE XXVIII

Capillary Viscometer Results on Aged VP/Am/MMA Terpolymers		
Approximate Temp. F ^a	1% MMA ^b	5% MMA ^b
105	4.00	3.27
130	3.02	2.32
155	2.01	1.69
185	1.34	1.19
205	0.92	0.85
230	0.61	0.61
255	0.42	0.43
280	0.31	0.34
305	0.25	0.26

^aTemperature of viscosity measurement.
^bTerpolymerization was carried out in synthetic seawater.

Referring to the results in Table XXVIII, it is evident that the MMA level can be as high as at least 5 weight percent without adversely affecting solution viscosity or thermal stability of the terpolymer systems. In the temperature range of 105 F to 205 F., the viscosity of

the terpolymer system containing 1 wt percent MMA was slightly higher than that of the 5 wt percent MMA system.

EXAMPLE XIX

Thermal Stability of Unaged Terpolymers

This example compares the thermal stability of 0.25 weight percent solution of unaged VP/Am/MMA terpolymers (49.5/49.5/1.00 weight percent) as evidenced by solution viscosities determined by capillary viscometry. One of the terpolymers was prepared in deionized water whereas the other terpolymer was prepared in synthetic seawater. Results are summarized in Table XXIX.

TABLE XXIX

Solution Viscosities of VP/Am/MMA Terpolymers by Programmed Capillary Viscometry		
Approximate Temp. F ^c	Viscosity (cP)	
	1% MMA ^a	1% MMA ^b
105	3.65	2.62
130	2.81	1.95
155	1.99	1.48
185	1.48	1.07
205	1.10	0.93
230	0.92	0.76
255	0.69	0.61
280	0.57	0.50
305	0.46	0.44

^aPrepared in synthetic seawater
^bPrepared in deionized water
^cTemperature of viscosity measurement

Referring to the results in Table XXIX, it is evident that the viscosities in the polymer system containing the terpolymer prepared in synthetic seawater are somewhat higher than the viscosities observed in the system containing the terpolymer prepared in deionized water.

EXAMPLE XX

Viscosities of Solutions Containing VP/Am/X Terpolymers by Programmed Capillary Viscometry

This example discloses temperature-programmed capillary viscometer results on 0.25 weight percent solutions of control terpolymers consisting of N-vinyl-2-pyrrolidone (VP) and acrylamide (Am) and a third monomer X (1 wt percent) selected from the group of methyl acrylate (MA), butyl acrylate (BA), hydroxyethyl acrylate (HEA), lauryl methacrylate (LMA), acrylonitrile (AN), vinyl acetate (VA), styrene (STY), 4-vinylpyridine (4-VPy), 5-methyl-2-vinyl pyridine (MVPy) and mixtures thereof. Solutions were aged for 7 days at 300 F before carrying out the capillary viscosity measurements. Results are summarized in Table XXX. The terpolymers were prepared in 0.7 ionic strength aqueous sodium chloride solution initiated by 0.25 wt percent AIBN (based on total monomers). Although not prepared in polymerization media comprising mixed salts or synthetic sea water, as preferred for the inventive polymers, the properties of these terpolymers are expected to reflect the influence of the different monomers used. The properties of terpolymers prepared in preferred media, e.g. SSW, should be similarly affected by the type and amount of monomer used. Each terpolymer resulted from a reactor charge of 49.5 wt percent VP, 49.5 wt percent Am and 1.0 wt percent of the monomer designated in Table XXX.

TABLE XXX

Solution Viscosities of Aged Terpolymers VP/Am/X ^a										
Viscosity (cP)										
Approximate Temp. F ^b	(MA) ^c	(BA) ^d	(HEA) ^e	(LMA) ^f	(AN) ^g	(VA) ^h	(STY) ⁱ	(4-VPy) ^j	(MVPy) ^k	T ^l
85	3.37	3.44	1.67	1.3	3.13	1.05	3.75	4.2	4.3	3.30
145	1.62	1.57	0.81	0.61	1.82	0.7	2.0	2.65	2.0	1.97
180	0.79	0.99	0.61	0.56	1.10	0.44	1.09	1.49	1.25	1.31
225	0.47	0.64	0.40	0.40	0.60	0.32	0.58	0.65	0.7	0.55
250	0.31	0.43	0.38	0.37	0.43	0.26	0.38	0.50	0.48	0.40
275	0.21	0.40	0.3	0.32	0.27	0.23	0.25	0.34	0.33	0.30
300	0.37	0.60	NM ^m	NM ^m	0.26	0.22	0.19	0.34	0.21	0.26

^aX represents termonomer as defined in footnotes a through j.
^bMA represents methyl acrylate
^cBA represents butyl acrylate
^dHEA represents hydroxyethyl acrylate
^eLMA represents lauryl methacrylate
^fAN represents acrylonitrile
^gVA represents vinyl acetate
^hSTY represents styrene
ⁱ4-VPy represents 4-vinylpyridine
^jMVPy represents 3-methyl-2-vinyl pyridine
^kT represents a 1:1 wt/wt mixture of methyl methacrylate (MMA) and vinyl acetate (VA)
^lTemperature of viscosity measurement
^mNM represents Not Measured

Referring to the results in Table XXX, it is evident that the initial viscosities of the thermally aged system containing hydroxyethyl acrylate (HEA), lauryl methacrylate (LMA), and vinyl acetate (VA) termonomers were significantly lower than systems containing the other designated termonomers. Perhaps this indicates the greater inherent tendency of the pendant moieties in these three terpolymers to hydrolyze during the 7 day thermal aging at 300 F before measuring solution viscosities by programmed capillary viscometry. All of the systems in Table XXX showed greatly reduced viscosities at elevated temperatures, particularly at temperatures above 180 F. However, these viscosities are still greater than that of synthetic sea water at comparable temperatures. At temperatures up to 250 F, higher viscosities were exhibited by systems containing pyridine-derived termonomers such as 4-vinylpyridine (4VPy) and 3-methyl-2-vinylpyridine (MVPy).

This observation perhaps is related to the fact that the pyridine moiety is probably the least readily altered grouping under the test conditions. A similar rationale may account for the less dramatic effects in the terpolymer systems derived, respectively, from VP, Am and styrene; and VP, Am and acrylonitrile (AN). In general, the test conditions appear severe enough to cause significant hydrolysis of pendant ester moieties.

Calculations show that between 85 F and 300 F, the terpolymer containing MA lost 89.6 percent of its viscosity and the BA terpolymer lost 82.6 percent of its viscosity, while the terpolymers containing 4-VPy and MVPy lost 94.3 and 95.1 percent, respectively, of their viscosities.

EXAMPLE XXI

Viscosities of Unaged Terpolymers

This example discloses viscosities of unaged 0.25 weight percent solutions containing VP/Am/MMA terpolymers. Terpolymers contained methyl methacrylate (MMA) at levels of 0.25 to 10 weight percent, with the balance of the terpolymer consisting of equal weights of units derived from N-vinyl-2-pyrrolidone (VP) and acrylamide (Am). Relative viscosities as well as Brookfield viscosities are presented for the series of control terpolymer compositions prepared in 0.7 ionic strength aqueous sodium chloride solution. Brookfield viscosities are given for similar control terpolymer

compositions prepared in deionized water and selected inventive terpolymers prepared in synthetic seawater. Results are summarized in Table XXXI.

TABLE XXXI

Viscosities of Unaged Terpolymer Solutions					0.7 Ionic Strength ^a Terpolymer Relative Viscosity ^d
Wt % MMA ^e	Deionized H ₂ O ^b Terpolymer Viscosity (cP)	0.7 Ionic Strength ^c Terpolymer Viscosity (cP)	Synthetic Seawater Terpolymer Viscosity (cP)		
0.25	3.6	5.1	NM ^f		1.79
0.50	3.9	5.1	NM ^f		1.74
1.0	3.8	5.4	5.3		1.73
2.0	3.7	5.1	NM ^f		1.67
3.0	3.6	4.5	5.1		1.56
5.0 ^g	3.6	4.6	5.0		1.57
7.0 ^g	3.4	4.7	NM ^f		1.63
10.0 ^g	3.0	4.4	NM ^f		1.48

^aBalance of terpolymer composed equal weight proportions of VP and Am units.
^bTerpolymer was prepared in deionized water.
^cTerpolymer was prepared in 0.7 ionic strength aqueous sodium chloride solution.
^dTerpolymer was prepared in synthetic seawater.
^eRelative viscosity is calculated by dividing the time required for a solution to pass through a capillary viscometer by the time required for the solvent to pass through the same capillary viscometer.
^fSample contained haze or water insoluble material.
^gSample more heavy than that referenced in footnote e; contained a considerable amount of water insoluble material.
^hSample contained a white precipitate.
ⁱNot measured.

Referring to the results in Table XXXI, it is evident that the viscosities of the control terpolymers prepared in the 0.7 ionic strength aqueous sodium chloride solution and the inventive terpolymers prepared in synthetic seawater were somewhat higher than the measurements for the control terpolymers prepared in deionized water. It is noteworthy that the terpolymer compositions containing less than 1 weight percent methyl methacrylate (MMA) imparted significant viscosities to water solutions of electrolytes. As noted in footnotes f, g, and h of Table XXXI, attention is called to the fact that terpolymer compositions containing more than about 5 weight percent methyl methacrylate (MMA) exhibited greatly reduced water solubilities.

EXAMPLE XXII

Radiation Polymerization in SOW

A series of VP/Am copolymers was prepared in substitute ocean water at about 80 F (27° C.) under an argon atmosphere by irradiation with gamma rays from a cobalt 60 source having a maximum dose rate of about 5 MRad/hour. Three of the samples were 10 weight percent each Am and VP and 80 weight percent SSW (50/50 VP/Am). The remaining 20 samples were each 12 weight percent Am, 18 weight percent VP and 70 weight percent SOW. The substitute ocean water employed was made using the sea salt described in Table I at a concentration of about 4.2 weight percent, with a

could be expected to be higher, while at higher concentrations the K values should be lower. To estimate such K values, the values obtained at a concentration of 0.25 g/dL could be extrapolated using the slopes of the existing curves for similar copolymers.

The relative weights of the monomers and SOW employed, the total dose given each sample and corresponding dose rate employed, the percent conversion obtained, the Brookfield, inherent and relative viscosities of each copolymer prepared and the calculated K values are given in Table XXXII. Conversion of monomers to copolymers were determined in each run by either NMR and/or gravimetric practices as known in the art. Conversions ranged from 90 to 100 percent.

TABLE XXXII

Sample No. ^(a)	Weight Percent			Total Dose		Dose Rate	Percent Conversion	Viscosities		Calculated K Value
	AM	VP	SOW	kRad	kRad/hr			Relative	Inherent dL/g	
1	10	10	80	14.0	18.9	90	2.31	3.35	135.9	
2	10	10	80	48.0	18.9	95	3.40	4.94	166.6	
3	10	10	80	48.0	33.1	97	3.22	4.68	162.6	
4 ^(b)	12	18	70	107.6	47.7	96	—	—	—	
5	12	18	70	48.0	33.0	90	3.61	5.13	170.9	
6	12	18	70	48.0	63.8	96	3.51	5.02	168.9	
7 ^(b)	12	18	70	144.0	63.8	100	—	—	—	
8	12	18	70	30.0	958	90	3.01	4.41	157.5	
9	12	18	70	30.0	4730	99	2.48	3.63	142.0	
10	12	18	70	100.0	600	95	3.41	4.91	166.8	
11 ^(b)	12	18	70	200.0	600	95	—	—	—	
12 ^(c)	12	18	70	100.0	600	95	3.91	5.45	176.5	
13 ^{(d)(h)}	12	18	70	200.0	600	96	—	—	—	

Notes:
(a) Volumes show for samples 1 to 3 in 1 liter for remainder in 2 liters.
(b) Crystallized, sample did not completely dissolve.
(c) Initial temperature before irradiation about 48 F (9 C.)
(d) Initial temperature before irradiation about 32 F (1 C.)
(h) A dash signifies no determination made.

calculated ionic strength of about 0.8

Each sample solution was contained in a closable polyethylene bag, the sample was degassed by bubbling argon through it to displace the air and the bag was closed. Each bag was placed into an open top paste board box for convenience during the irradiation process and for late processing. To insure more even penetration of the gamma rays into the sample each sample was irradiated for about half of the total exposure time on each side by turning the sample 180° midway through the process. Each comonomer-SOW solution was converted into a viscous mass of water soluble copolymer (gel log) by the irradiation unless specified otherwise.

Relative viscosities of each sample were determined at 25° C. in a No. 1 Ubbelohde viscometer as 0.25 weight percent copolymer in SSW.

Inherent viscosities were determined from relative viscosities by employing the conventional relationship

$$\text{inherent viscosity} = \frac{\ln(\text{relative viscosity})}{\text{concentration (g/dL)}}$$

K values of each sample were calculated as described in Example VIII from the relative solution viscosities. Since all viscosities herein were measured for solutions of 0.25 weight percent copolymers (equivalent to 0.25 gram/deciliter), to compare the K values computed therefrom with other K values it may be desirable to compensate for copolymer concentration. That is, as seen by the curves in FIG. 8, at concentrations of less than 0.25 g/dL the K values for the same copolymers

The results in Table XXXII indicate the molecular weights of the various copolymers prepared by gamma irradiation in SOW, as reflected by the inherent viscosity data, are related to concentration of the monomers, total dose given the system, the dose rate used and polymerization temperature. For the 50/50 VP/Am copolymers prepared at a total monomer concentration of 20 weight percent, the low inherent viscosity of 3.35 dL/g and K value of about 136 obtained with a total dose of 16 kRad and a dose rate of about 19 kRad/hr for sample 1 show substantially lower viscosity compared to samples 2 and 3. However, sample 2 shows an inherent viscosity of 4.94 dL/g and K value of about 167. The dose rate was the same as for example 1 but the total dose was tripled to 48 kRad. On the other hand, the inherent viscosity of 4.68 dL/g and K value of about 163 obtained with sample 3 shows that maintaining a medium total dose of about 48 kRad coupled with a higher dose rate of about 33 kRad/hr has yielded a slightly less desirable copolymer (lower viscosity) for EOR than that of sample 2.

Similarly, inspecting the conditions used and results obtained for samples 4 to 13, the 60/40 VP/Am copolymers, a similar trend is noted. For example, sample 5 shows that a medium dose rate of about 33 kRad/hr coupled with a medium total dose of 48 kRad yields a copolymer having an inherent viscosity of about 5.13 dL/g and K value of about 171. The total monomer concentration in preparing samples 4 to 13 was 30 weight percent. This concentration and/or difference in VP/Am weight ratio has apparently shifted the most

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desirable dose rate from about 19 kRad/hr for sample 2 to about 33 kRad/hr for sample 5

In comparing inherent viscosities and K values of sample 6 (5.02 dL/g and 169), sample 8 (4.41 dL/g and 158) and sample 9 (3.63 dL/g and 142) with those of sample 5 (5.13 dL/g and 171), it is noted that all samples received a medium total dose of 48 to 50 kRad. However, increasing the dose rate from a medium value of about 33 kRad/hr to higher values ranging from about 64 to 4700 kRad/hr resulted in the formation of copolymers having decreasing inherent viscosities, i.e. The higher the dose rate under these conditions, the lower the polymer viscosity. The irradiation applied in the preparation of samples 4 and 7 was excessive and crosslinking was noted, e.g. insoluble or nearly insoluble polymers were made.

The effects of total dose at a high dose rate of 600 kRad/hr and polymerization temperature are shown in the results obtained for samples 10-13. The inherent viscosity of 4.91 dL/g and K value of about 167 obtained for sample 10, at total dose of 100 kRad and polymerization temperature of about 80 F, is somewhat lower than the inherent viscosity of 5.45 dL/g and K value of about 176 obtained for sample 12 at a total dose of 100 kRad and polymerization temperature of about 48 F. This suggests that the molecular weight of the copolymers can be increased by decreasing the polymerization temperature to a temperature below ambient, provided that freezing of the system is avoided. The temperature can be lowered prior to, during or after irradiation. This temperature will vary, depending upon the concentration of monomers and the nature of the polymerization medium. For the monomer concentrations and polymerization medium employed in this Example, a minimum temperature of about 20 F can be employed. The results obtained for samples 11 and 13 indicate that the total dose of 200 kRad was excessive under the conditions employed. Thus, some crosslinking (gelation) occurred and the polymer samples did not dissolve enough to obtain meaningful viscosity values and K values.

In this Example, the results show that the copolymer

ably in EOR. Manipulation of total dose, dose rate, temperature and other variables can be practiced as need to obtain polymers having the desired properties for the end uses contemplated. Polymerization is most desirably carried out in the absence of molecular oxygen. Similar selected doses/dose rates or conditions can be used for preparing these polymers in the tertiary alkanol media referred to elsewhere herein.

EXAMPLE XXIII

Vp-Am Copolymers as Flocculants

Several invention copolymers and several commercially available polymers as controls were tested for efficacy as flocculating agents in Caney River (Oklahoma) water containing 250 ppm added bentonite clay of 325 mesh particle size. The river water had an initial turbidity of about 87 nephelos units. The procedures of ASTM-D 2035-80 and ASTM Standards cited therein were followed.

The inventive copolymers consisting of VP/Am weight ratios of 40/60, 30/70 and 20/80 were prepared in SSW at 49 C. in the presence of 0.5 weight percent AIBN based on the weight of the monomers. A portion of each copolymer was subsequently diluted with SSW to form a 1 weight percent solution and the Brookfield viscosities of the solutions were determined at 25 C. at 6 rpm.

Sample 1, 40/60 VP/Am, had a Brookfield viscosity of about 73 cP as determined with a U.L. spindle.

Sample 2, 30/70 VP/Am, had a Brookfield viscosity of about 157 cP as determined with a No. 1 spindle.

Sample 3, 20/80 VP/Am, had a Brookfield viscosity of about 232 cP determined with a No. 1 spindle.

In the procedure followed, each 1500 mL jar, containing 1000 mL of the water-clay mixture and 0.5 ppm of the test polymer based on the contents of the jar, was stirred for 1 minute at a flash mix speed of 105 rpm. The speed was reduced to 20 rpm and stirring continued for 20 minutes. The stirrer was withdrawn and results then determined in accordance with the ASTM procedure except for color of the water which was not recorded. The results are set forth in Table XXXIII.

TABLE XXXIII

Remarks	VP/Am Copolymer As Flocculating Agents						Controls ^(a)	
	Invention						7 ^(b)	8 ^(c)
	1	2	3	4	5	6		
Run No.	40/60	VP/AM	30/70	VP/Am	20/80	VP/Am	1125L	1180
Sample Description								
Initial sample pH	7.11	7.11	7.11	7.11	7.11	7.06	7.06	7.06
Initial turbidity nephelos units	87	87	87	87	87	87	86	86
Test temp. C.	27.2	27.2	27.2	27.2	27.2	27.2	23.8	23.8
Time, first flocc, min.	0.5	0.5	0.5	0.5	0.5	0.5	0.1	0.5
Floc size	medium	medium	medium	medium	medium	medium	coarse	medium
	fine	fine	fine	fine	fine	fine		fine
Settling rate, mm.	5.5	5.5	5.5	5.5	5.5	5.5	0.2	4.0
Turbidity 15 min, settle; nephelos	2.9	3.0	3.5	3.8	3.4	3.2	3.8	1.5
Final sample pH	7.15	7.14	7.21	7.20	7.27	7.31	7.69	6.83

^(a)Results are averages of 2 runs.
^(b)Betz Poly-Floc @ 1125L, Betz Laboratories, Inc., Trevose, PA.
^(c)Betz Poly-Floc @ 1180.

having the highest inherent viscosity (5.45 dL/g) was made at 52 F by irradiating the monomer solution to obtain a total dose of 100 kRad by employing a dose rate of 600 kRad/hr. This copolymer would be expected to provide acceptable performance in EOR. In addition, copolymers having somewhat lower inherent viscosities, e.g. 5.13 dL/g and 5.02 dL/g, were made by employing total doses and dose rates of 48 kRad and 33 kRad/hr and 48 kRad and about 64 kRad/hr. These copolymers would also be expected to perform credit-

The results obtained with the inventive copolymers are comparable to those obtained with commercial flocculant, Betz Poly-Floc @ 1180. Although the tests were conducted in river water containing an unknown concentration of dissolved salts (The water is considered to be hard water based on its reaction with soap), it is expected that the inventive copolymers will serve as effective flocculating agents for processes involving the

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clarification of water containing suspended matter. Specific applications might be in clarification of brackish water, removal of fines in mineral processing; i.e., phosphate mining, uranium or copper mining, or removal of clay from potash ores suspended in concentrated brines.

EXAMPLE XXIV

Comparative Properties of Polymers Prepared by Radiation Polymerization in SOW and H₂O

A series of VP/Am copolymer was prepared in substitute ocean water at about 80 F (27° C.) under an argon atmosphere by irradiation with gamma rays from a cobalt 60 source employing a dose rate of about 2530-2600 KRad/hour. These samples were each 18 weight percent VP, 12 weight percent Am and 70 weight percent H₂O (control) or SOW (invention) (60/40 VP/Am). The substitute ocean water employed was made using the sea salt described in Table I at a concentration of about 4.2 weight percent, with a calculated ionic strength of about 0.8.

Each sample solution was contained in a closable polyethylene bag, the sample was degassed by bubbling

solutions of 0.1 and 0.25 weight percent copolymers (equivalent to 0.1 or 0.25 gram/deciliter), to compare the K values computed therefrom with other K values it may be desirable to compensate for copolymer concentration. That is, as seen by the curves in FIG. 8, at concentrations of less than 0.25 g/dL the K values for the same copolymers could be expected to be higher, while at higher concentrations the K values should be lower. To estimate such K values, the values obtained at concentration of 0.1 or 0.25 g/dL could be extrapolated using the slopes of the existing curves for similar copolymers.

The relative weights of the monomers and SOW polymerization medium employed, the total dose given each sample and corresponding dose rate employed, the percent conversion obtained, the concentrations used for testing the Brookfield, calculated inherent and relative viscosities of each copolymer prepared and the calculated K values are given in Table XXXIV. Conversion of monomers to copolymers was determined in each run by gravimetric practices as known in the art. Conversions ranged from 95 to 100 percent.

TABLE XXXIV

Radiation Conditions Employed and Results Obtained for Copolymers										Viscosities		
Sample No.	Invention/Control	Weight Percent			Total Dose kRad	Dose Rate kRad/hr	Percent Conversion	Concentration, Wt. Percent	Brookfield cP	Relative	Inherent dL/g	Calculated K Value
		PV	Am	Medium ^b								
1	I ^a	18	12	70(SOW)	100	2600	95	0.25	— ^c	3.18	4.63	161.7
2	I	18	12	70(SOW)	100	2530	99.7	1.0	48	—	—	—
2	I	18	12	70(SOW)	100	2530	99.7	0.1	—	1.71	5.19	171.8
2	I	18	12	70(SOW)	100	2530	99.7	0.25	—	3.24	4.69	163.1
3	C ^d	18	12	70(H ₂ O)	100	2530	100	1.0	24	—	—	—
3	C	18	12	70(H ₂ O)	100	2530	100	0.1	—	1.60	4.67	160.3
3	C	18	12	70(H ₂ O)	100	2530	100	0.25	—	2.88	4.13	154.1

Notes:
^aVolume dose for samples 1 to 3 was 1 liter.
^bSubstitute Ocean Water (SOW) or distilled water (H₂O), as indicated.
^cA dash signifies no determination made.
^dInvention polymer.
^eControl polymer.

argon through it to displace the air and the bag was closed. Each bag was placed into an open top paste board box for convenience during the irradiation process and for later processing. To insure more even penetration of the gamma rays into the sample each sample was irradiated for about half of the total exposure time on each side by turning the sample 180° midway through the process. Each comonomer-SOW solution was converted into a viscous mass of water soluble copolymer (gel log) by the irradiation.

The Brookfield viscosity of each sample diluted in 0.7 Ionic Strength SSW (as described earlier herein) was determined at 25° C. at 6 rpm using a #1 spindle. The diluted sample was prepared by dissolving 16.50 g gel in 483.3 g SSW, equivalent to about 1.0 weight percent copolymer.

Relative viscosities of each sample were determined at 25° C. in a No. 1 Ubbelohde viscometer as 0.1 and 0.25 weight percent copolymer in SSW.

Inherent viscosities were determined from relative viscosities by employing the conventional relationship

$$\text{inherent viscosity} = \frac{\ln(\text{relative viscosity})}{\text{concentration (g/dL)}}$$

K values of each sample were calculated as described in Example VIII from the relative solution viscosities. Since the relative viscosities herein were measured for

Samples 1 and 2 of inventive polymers were prepared in different batches with the same monomer proportions and reaction conditions, except for a slightly different radiation dose rate. The values obtained for relative and inherent viscosities at concentrations of 0.25 weight percent correlate closely. Comparing sample 2 (prepared in SOW) to control polymer sample 3 (prepared in H₂O), at a concentration of 1.0 weight percent, a Brookfield viscosity twice as high was obtained for sample 2. At a concentration of 0.1 weight percent, the relative viscosity was about 7 percent higher and the inherent viscosity was about 10 percent higher for inventive polymer sample 2, prepared in SOW. Similarly, when tested at concentrations of 0.25 weight percent, the sample 2 solution gave a relative viscosity about 13 percent higher and an inherent viscosity about 14 percent higher than those obtained from sample 3, prepared in H₂O.

The K values for the inventive polymer sample 2 (SOW) solution were about 11 units higher than those for sample 3 (H₂O) solution when tested at 0.1 weight percent concentration, and about 9 units higher when tested at 0.25 weight percent. This further indicates the superiority of the polymers prepared in accordance with the invention (in SOW) compared with those prepared in H₂O (control). The greater numerical difference in K values observed at the lower concentration is consistent with the variation in K value with concentra-

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tion, noted in Example VIII. The K values obtained for sample 3 at concentrations of 0.1 and 0.25 weight percent can be plotted on a graph such as FIG. 8 to form a line approximately parallel to the lower curve for 50:50 VP/Am copolymers prepared in H₂O. By extrapolating this line to a concentration of 1.0 weight percent (approximately equivalent to 1.0 grams/deciliter), a K value of about 135-140 can be estimated, which is typical of superior polymers of the prior art. However, by plotting K values for sample 2 and extrapolating in the same manner, an estimated K value of at least about 145-150 is obtained.

Thus, the use of a polymerization medium containing electrolytes, preferably a mixture of electrolytes as in the SOW or SSW described herein, in preparing the polymers of this invention by radiation polymerization improves their viscosity properties, analogous to the results described in the previous examples for chemical initiation. Furthermore, other properties comprising cloud point and the resistance to loss of viscosity in hostile environments (high temperature, salinity and/or hardness) would also be improved, as shown in the previous examples when such polymerization media were used with chemical initiators. Thus, the use of radiation with polymerization media comprising mixed electrolytes, such as a synthetic sea water, is a preferred method of preparing the polymers of this invention because it is believed, based partly upon the work carried out thus far, that polymers produced according to the present invention using radiation initiation will produce polymers having a higher viscosity compared to chemical initiated polymers of the invention.

ADDITIONAL EXPERIMENTAL

The general experimental procedure used to prepare the polymers of the following examples involved the charging of monomers and water (either distilled water or saline water) to crown top bottles along with suitable initiators. The reaction mixtures were degassed with an inert gas for approximately 20 minutes before capping and allowing polymerization to take place at a specified temperature depending on the chemical initiator used. For radiation induced polymerizations, no chemical initiator was added and the reaction mixture in the crown top bottles was irradiated with suitable radiation dosages. At the end of the reaction period, the entire reaction mass was usually in the form of a gel.

Characterization of reaction products was carried out by addition of sufficient amounts of synthetic North Sea

water to the gel to prepare 0.1 weight percent and 0.25 weight percent polymer solutions for viscosity measurements. Relative viscosities of the 0.1 weight percent solutions at 25° C. were determined in a capillary viscometer. The unaged viscosities of the 0.25 weight percent polymer solutions were determined by high pressure capillary viscometry. In order to measure the aged viscosity of a polymer solution, the solution was aged in a sealed bomb at 300 F for 7 days as described hereinbefore. The aged viscosity of the sample was then determined by high pressure capillary viscometry. The formation of precipitate in the aging test indicated that the polymer lacked sufficient thermal stability in the hard salinity test medium to merit any further consideration as a mobility control agent in hostile environments (i.e., temperature 170° F, hardness cations > 500 ppm).

Since the viscosity of the synthetic North Sea water at 250° F was found to be on the order of 0.28 centipoise this value was used to indicate the relative effectiveness of the polymer solutions to mobilize crude oil over that which would be expected using sea water as a flooding medium.

The examples presented hereinbelow are representative of the instant teaching. Unless otherwise noted, the compositions were prepared and tested in accordance with the above general experimental procedure. Reaction times were usually on the order of 24 hours and reaction mixtures were usually neither stirred nor tumbled during the polymerizations. The total solids level generally was in the range of 5% to 50% with most of the preparations being carried out in the range of 20% to 35% total solids.

EXAMPLE XXV

NaAMPS Polymers For Hostile Environments

This example presents in summary form representative polymer compositions which are potentially useful as mobility control agents under hostile environment conditions. These samples are characterized by the presence of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) units. Solutions of these polymers in synthetic North Sea water (2500 ppm polymer) at 250 F exhibited unaged viscosities in the range of 1.30 to 7.05 centipoise. After thermal aging of these solutions in synthetic North Sea water at 300 F for 7 days, the aged viscosities of these solutions varied in the range of 1.28 to 4.59 centipoise. The viscosity of sea water at 250 F is about 0.28 centipoise.

TABLE XXXV

Hostile Environment Polymers Containing Sodium 2-Acrylamido-2-Methylpropanesulfonate (NaAMPS) Units									
Sample No	Wt. % NaAMPS ^a	Wt. % VP ^b	Wt. % Am ^c	Wt. % DMAm ^d	Inherent Viscosity (dL/g) ^e	Viscosity (cP) 250 F (2500 ppm)			
						Unaged	Aged	VR ^g	
1	100 ^f	0	0	0	11.04	7.05	4.59	16.4	
2	70 ^f	0	0	30	8.90	3.80	2.50	8.9	
3	55 ^f	30	15	0	9.01	2.19	1.83	6.6	
4	100 ^f	0	0	0	7.82	1.92	1.79	6.4	
5	100 ^f	0	0	0	7.59	2.43	1.42	3.1	
6	55 ^f	30	15	0	8.38	2.08	1.40	5.0	
7	70 ^f	0	0	30	7.85	2.07	1.37	4.9	
8	65 ^f	35	0	0	6.28	1.90	1.33	4.8	

TABLE XXXV-continued

Hostile Environment Polymers Containing Sodium 2-Acrylamido-2-Methylpropanesulfonate (NaAMPS) Units									
Sample No	Wt. % NaAMPS ^a	Wt. % VP ^b	Wt. % Am ^c	Wt. % DMAm ^d	Inherent Viscosity (dL/g) ^e	Viscosity (cP) 250 F (2500 ppm)			VR ^f
						Unaged	Aged		
9	25 ^g	30	25	0	8.19	1.56	1.28	4.6	

^aNaAMPS represents sodium 2-acrylamido-2-methylpropanesulfonate.
^bVP represents N-vinyl-2-pyrrolidone.
^cAm represents acrylamide.
^dDMAm represents N,N-dimethylacrylamide.
^eVR represents Viscosity Ratio and is calculated by dividing the aged viscosity of the polymer solution by 0.38 (the viscosity of sea water at 250° F.).
^fRefined grade 2-acrylamido-2-methylpropanesulfonic acid was neutralized to prepare the sodium salt (NaAMPS) used in synthesizing the polymers.
^gCommercial grade AMPS materials were used in these polymerizations.
^hIn this and subsequent examples, unless otherwise noted, viscosity was determined on 0.1 wt percent solutions in Synthetic North Sea Water at 25° C.

Referring to the results in Table XXXV, it is evident that the use of refined grade AMPS in homopolymer sample 1 (cf Nos 4 and 5) gave the homopolymer system with the highest aged viscosity, i.e., 4.59 cP compared to 1.79 cP (Sample No. 4) and 1.42 cP (Sample No. 5). these systems, respectively, exhibited aged viscosities which were 16.4, 6.4 and 5.1 times as viscous as sea water at 250° F.

Referring to samples 2 and 7, it is apparent that the 30/70 DMAm/NaAMPS copolymer (Sample 2) made with refined grade AMPS material exhibited a higher aged viscosity than did the copolymer prepared from commercial AMPS material (Sample 7).

The same conclusion applies to the three component polymer samples, numbers 3 (from refined grade AMPS) and 6 containing 30 weight percent VP, 15 weight percent acrylamide and 55 weight percent NaAMPS. Sample 9 (VP/Am/NaAMPS polymer 50/25/25) is another example of a polymer system which exhibited a significant aged viscosity value. In each three component polymer (i.e., samples 3, 6 and 9), the relative weight percent ratio of VP and Am was 2:1. In the course of this work, the weight ratio of VP to Am in three component polymer compositions is preferably not less than 1:1.

Referring to sample 8, it is evident that copolymers of VP and NaAMPS are useful in hostile environments for enhanced oil recovery: the aged viscosity at 250° F being 4.8 times the viscosity of sea water at 250° F.

Attention is called to the fact that the aged viscosities of samples 1-9 in Table XXXV were 4.6 to 16.4 times the viscosity of sea water at 250° F. Polymerfloods with such polymeric viscosifiers under hostile environment conditions would be expected to be significantly more effective in mobilizing crude oil than waterfloods with sea water.

EXAMPLE XXVI

Sodium 2-Acrylamido-2-Methylpropanesulfonate (NaAMPS) and Homopolymers of NaAMPS

This example describes the preparation of NaAMPS from refined grade 2-acrylamido-2-methylpropanesulfonic acid as well as the preparation and thermal aging of NaAMPS homopolymer. The low temperature VAZO 33 chemical initiator was used in the ambient temperature polymerization. VAZO 33 is 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile).

The sodium salt of 2-acrylamido-2-methylpropanesulfonic acid was prepared by dissolving 60 g of the sulfonic acid (refined grade) (0.29 mole) in an aerated alkaline solution which had been prepared by dissolving 12 g (0.3 mole) of sodium hydroxide in 60 g of distilled

water. The pH of the mixture at this point was approximately 13 and 0.89 g (4.3 mmoles) of 2-acrylamido-2-methylpropanesulfonic acid (refined grade) was added to adjust the pH to about 9. An additional 1.8 g of water was added to give a total mixture of about 135 grams (50 wt % NaAMPS). A 50 weight percent aqueous solution of NaAMPS monomer was routinely used as a stock solution for homopolymer, copolymer and three component polymer preparations.

A 60 g portion of a 50 weight percent aqueous solution of NaAMPS (30 g NaAMPS), 25.7 g distilled water and 15 mg of solid VAZO 33 was charged to a 10 ounce crown top bottle. After degassing the mixture with argon for 20 minutes, the bottle was capped and stored for 24 hours at ambient temperature. This reaction charge contained 35% total solids and 0.05 phm of initiator.

The gelled reaction mass was mixed with sufficient synthetic North Sea water to prepare 0.1 weight percent and 0.25 weight percent solutions of viscosity measurements. The homopolymer solution exhibited an inherent viscosity of 11.04 dL/g, an unaged viscosity of 7.05 centipoise and an aged viscosity of 4.59 centipoise. This aged viscosity is approximately 16 times greater than the viscosity of sea water at 250° F.

EXAMPLE XXVII

Poly(N-Vinyl-2-Pyrrolidone-co-Sodium-2-acrylamido-2-Methylpropanesulfonate)

This example describes the preparation of VP/NaAMPS copolymers containing, respectively, 25/75, 33/67 and 35/65 weight ratios of the respective comonomers. VAZO 33 was used as the initiator at a level of 0.10 phm in the first two runs and in the 35/65 run the initiator was 0.10 phm t-butyl hyponitrite.

For the 25/75 copolymer, a 45 g portion of a 50 weight percent solution of NaAMPS (prepared from commercial grade 2-acrylamido-2-methylpropanesulfonic acid), 97.5 g distilled water, 3.0 g VP and 4.5 g of a stock solution of initiator prepared by dissolving 0.267 g of VAZO 33 in 40 g VP was charged to a 10 ounce crown top bottle. After degassing the mixture with argon for 20 minutes, the bottle was capped and stored for 24 hours at ambient temperature. The reaction charge was 20% total solids. The 33/67 and 35/65 copolymers were similarly prepared.

The gelled reaction masses were individually mixed with sufficient synthetic North Sea water to give 0.1 weight percent and 0.25 weight percent solutions for

viscosity measurements. The results are shown in Table XXXVI

TABLE XXXVI

Aging Results on VP/NaAMPS Copolymers Aged in Synthetic North Sea Water			
Wt/Wt VP/NaAMPS	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
		Unaged	Aged
25/75	6.93	1.80	1.07
33/67	6.31	1.22	1.23
33/65	6.28	1.90	1.35

Referring to the results in Table XXXVI, it is evident that the aged viscosities of the copolymer solutions at 250° F were several times greater than the viscosity of sea water (0.28 cP) at 250° F. These copolymers, therefore, are potential candidates for polymerfloods in hostile environments.

EXAMPLE XXVIII

N-Vinyl-2-Pyrrolidone/Acrylamide/Sodium 2-Acrylamido-2-Methylpropanesulfonate Polymers

This sample describes the preparation of polymers of VP, Am and NaAMPS using VAZO ® 33 as the initiator (0.10 phm). Appropriate quantities of monomers were used to prepare VP/Am/NaAMPS polymers of the following compositions. 33/11/56; 25/10/65, 30/15/55, and 25/15/60

The gelled reaction masses were individually mixed with sufficient synthetic sea water to prepare 0.1 weight percent and 0.25 weight percent solutions for viscosity measurements. The results are summarized in Table XXXVII

TABLE XXXVII

Aging Results on VP/Am/NaAMPS Polymers Aged in Synthetic North Sea Water			
Wt/Wt/Wt VP/Am/NaAMPS	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
		Unaged	Aged
33/11/56	7.02	1.37	1.08
25/10/65	7.98	1.65	1.20
30/15/55	8.38	2.19	1.83
25/15/60	7.43	1.46	1.05

Referring to the results in Table XXXVII, it is apparent that the VP/Am/NaAMPS polymers are candidates for mobility control agent in hostile environments because the aged viscosities of the three component polymer solutions of 3.5 to 6.5 times the viscosity of sea water at 250° F indicates excellent stability. The weight ratio of VP to Am in these hostile environment terpolymers varied over the range of 1.66:1 to 3:1 in these 250 F tests. At temperatures of 250 F and above a ratio of at least 1:1 N-vinyl lactam-unsaturated amide is preferred. A lower ratio, for instance as low as 0.11:1 can be used in lower temperature applications such as at 170 F

EXAMPLE XXIX

Polymerization With Low Temperature Initiator

This example demonstrates that copolymers and three component polymers of NaAMPS as well as VP/Am copolymers can be prepared with tertiary butyl hyponitrite as the chemical initiator. These preparations were carried out in essentially the same manner as the runs using VAZO ® 33 and the inherent viscosities of the reaction products were of the same order of

magnitude as observed in the VAZO ® 33 runs. The aged viscosities of several VP/Am copolymers are shown in Table XXXVIII

TABLE XXXVIII

Solution Viscosities of Polymers Initiated by Tertiary Butyl Hyponitrite (Measured in Synthetic North Sea Water)			
Wt/Wt/Wt VP/Am/NaAMPS	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
		Unaged	Aged
60/40/0	10.31 (5% T.S.) ^a	2.82	1.23
60/40/0	9.18 (20% T.S.) ^a	1.33	1.05
60/40/0	7.36 (30% T.S.) ^a	1.39	0.86
30/15/55	7.60	NM ^a	NM ^a
30/18/52	7.58	NM ^a	NM ^a
30/20/50	7.51	NM ^a	NM ^a
30/0/70	6.27	NM ^a	NM ^a
15/0/65	6.28	1.50	1.35
PVP/PAm (60/40) ^b	NM ^a	0.97	Pptd ^c

^aNM represents Not Measured.

^bT.S. represents total solids.

^cThis control sample was prepared by blending 60 parts by weight of polyvinyl pyrrolidone with 40 parts by weight of polyacrylamide.

^dThe solution of the PVP/PAm homopolymer blend failed the high temperature aging test as evidenced by the formation of a precipitate.

The results on the 60/40 VP/Am copolymers in Table XXXVIII indicate that initiation with tertiary butyl hyponitrite gave copolymers which did not precipitate on aging and exhibited aged solution viscosities at 250 F which were at least several times the viscosity of sea water at 250 F. By contrast, a 60/40 wt/wt blend of PVP/PAm homopolymers failed the thermal aging test as evidenced by precipitate formation.

Referring to the NaAMPS derived polymers in Table XXXVIII, it is evident that the polymers exhibited inherent viscosities which are similar in magnitude to those polymers prepared hereinabove by VAZO ® 33 initiation.

EXAMPLE XXX

N-Vinyl-2-Pyrrolidone/Acrylamide/Diacetone Acrylamide Polymers (VP/Am/DAAm)

This example describes the preparations and testing of VP/Am/DAAm polymers. The polymerizations were carried out either in synthetic sea water or distilled water in accordance with the general experimental procedure described hereinabove (20% total solids, VAZO ® 33 initiator at 0.06±0.015 phm).

The gelled reaction masses were individually dissolved in sufficient synthetic North Sea water to give 0.1 weight percent and 0.25 weight percent polymer solutions for viscosity measurements. Results are summarized in Table XXXIX.

TABLE XXXIX

Aging Results on VP/Am/DAAm Polymers Aged in Synthetic North Sea Water			
Wt/Wt/Wt VP/Am/DAAm	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
		Unaged	Aged
50/45/5	8.58	1.54	0.74
50/43/7	7.48	1.20	0.84
50/40/10	6.63 ^a	1.09	0.89
50/35/15	6.33 ^a	1.03	0.97
48/38/14	7.44	1.66	0.97
45/45/10	8.21	1.72	0.90
40/50/10	7.40 ^a	2.04	Pptd ^b

TABLE XXXIX-continued
Aging Results on VP/Am/DAAm Polymers
Aged in Synthetic North Sea Water

Wt/Wt/Wt VP/Am/DAAm	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
		Unaged	Aged
30/30/20	7.18 ^a	1.93	Fp ^b

^aInherent viscosities were determined on 2500 ppm polymer solutions in synthetic North Sea water.

^bThese samples failed the hostile environment thermal aging tests because precipitates formed in the polymer solutions.

Referring to the results in Table XXXIX, it is evident that the first six entries performed well in the thermal aging tests exhibiting aged viscosities on the order of 2.5 to 3.5 times the viscosity of synthetic sea water at 250° F. The last two entries of Table XXXIX failed to perform well in the thermal aging tests resulting in the formation of precipitates.

In regard to the last two entries of Table XXXIX, it should be noted that the weight ratio of N-vinyl-2-pyrrolidone to acrylamide in the three component polymers was less than 1:1. Referring again to the first six three component polymers of Table XXXIX, it should be noted that the weight ratio of N-vinyl-2-pyrrolidone to acrylamide varied over the range of 1:1 to about 1.4:1 in these 250° F tests. At temperatures of 250° F and above a ratio of at least 1:1 N-vinyl lactam-unsaturated amide is preferred. A lower ratio, for instance as low as 0.11:1 can be used in lower temperature applications such as at 170° F. This observation suggests that thermal stabilization of the three component polymer systems is related to the weight ratio of VP to Am in the polymer.

EXAMPLE XXXI

Homopolymerization of NaAMPS

This example describes the homopolymerization of NaAMPS without the addition of any conventional chemical initiator. In this procedure advantage is taken of the fact that the free acid, 2-acrylamido-2-methylpropanesulfonic acid spontaneously polymerizes in the presence of water and/or initiates the polymerization of NaAMPS in aqueous solution.

To a solution of 43.6 g of NaOH (1.09 moles) of 230.5 g of distilled water was added 226.0 g (1.0904 moles) of 2-acrylamido-2-methylpropanesulfonic acid (commercial grade) slowly with stirring. With external cooling and a slow rate of addition, the temperature was maintained at 30° C. or below. The concentrated solution was transferred to a stoppered flask and kept at room temperature for 30 minutes. The flask was then cooled to 5° C. for 48 hours. A high viscosity clear gel was obtained. Optionally, the homopolymerization may be carried out by substituting either a saline or a sea water formulation for the distilled water.

The homopolymer solution in synthetic North Sea water exhibited an inherent viscosity of 7.39 dL/g; and

unaged viscosity of 2.45 cP and an aged viscosity of 1.42 cP (see sample number 5 in Table XXXV).

EXAMPLE XXXII

5 Poly(N-Vinyl-2-Pyrrolidone-cl-Sodium-2-Acrylamido-2-Methylpropanesulfonate) Initiated by Radiation

This example describes the copolymerization of NaAMPS and VP initiated by cobalt 60 irradiation. The NaAMPS monomer was prepared by the neutralization of commercial grade 2-acrylamido-2-methylpropanesulfonic acid.

A 354 g portion of a 50 weight percent aqueous solution of NaAMPS, 220 g of distilled water and 87 g N-vinyl-2-pyrrolidone were placed in a 26 ounce crown top bottle. After degassing the mixture for 20 minutes with argon, the bottle was capped. The reactor charge contained 40 weight % total solids. Polymerization was initiated by using a dose rate of 100 Krad/hour for 0.4 hour (dose of 40 Krad). The viscous reaction mass was dissolved in sufficient synthetic North Sea water to give a 0.25 weight percent solution of copolymer for viscosity measurements.

The inherent viscosity of the copolymer solution was 6.05 dL/g at 25° C. The unaged viscosity was 1.30 centipose and the aged viscosity was 1.2 centipose. This aged viscosity is about 4.3 times the viscosity of sea water at 250° F. Copolymers of NaAMPS and VP initiated by irradiation are potentially useful as mobility buffers in hostile environments.

EXAMPLE XXXIII

Preparation of VP/Am Copolymers by Radiation Initiation

This example describes the preparation of VP/Am copolymers [poly(N-vinyl-2-pyrrolidone-co-acrylamide)] in synthetic sea water with radiation initiation. The samples of 50/50 wt/wt copolymers were prepared at 20% total solids and the samples of 60/40 wt/wt copolymers were prepared at 30% total solids. The reaction mixture were charged to crown top bottles, degassed with argon and capped. The bottles were exposed to gamma radiation from a Co⁶⁰ source at the intensity and dosage noted in Table XL below. Polymerization was signaled by warming of the reaction mixture (reaction exotherm) and the thickening of the reaction mass to a gel.

The gelled reaction masses were individually dissolved in synthetic sea water to give 1000 ppm copolymer solutions for determining relative and inherent viscosities at 25° C. Additional copolymer solutions were prepared at 2500 ppm for thermal aging study. The relative and inherent viscosities were determined from measurements made in a capillary viscometer. The unaged viscosities of the 2500 ppm copolymer solutions were determined by high pressure capillary viscometry at 250° F. The copolymer solutions (2500 ppm) were aged for seven days at 300° F before determining aged viscosities by high pressure capillary viscometry at 250° F. Results are summarized in Table XL.

TABLE XL

Aging Results on VP/Am (Radiation Initiated) Copolymers Aged in Synthetic North Sea Water							Viscosity (cP) 250° F (2500 ppm)	
Wt/Wt VP/Am	% Total Solids	K Value	Intensity Krad/hr	Dose Krad	Inherent (dL/g)		Unaged	Aged
50/50	20	204	24	14	7.46		1.93	0.80
50/50	20	213	100	40	8.13		1.86	0.93

TABLE XL-continued

Aging Results on VP/Am (Radiation Initiated) Copolymers Aged in Synthetic North Sea Water							Viscosity (cP)	
Wt/Wt VP/Am	% Total Solids	K-Value	Intensity Krad/hr	Dose Krad	Inherent (dL/g)	250 F (2500 ppm)		
							Unaged	Aged
60/40	30	100	50	38	7.17	1.32	0.89	
60/40	30	199	50	46	7.14	1.48	0.96	
60/40	30	190	80	40	6.48	1.35	0.96	
60/40	30	204	80	48	7.44	1.29	0.84	
SNBW*	—	—	—	—	—	—	—	0.28

*SNBW represents synthetic North Sea water

Referring to the aged viscosities in the above table, it is evident that the copolymer solution values were 3 to 3.5 times the viscosity of synthetic sea water at 250° F. The slightly higher inherent viscosities of the 50/50 copolymers is attributable to the higher percentage of acrylamide units compared to the 60/40 copolymer. The whole range of radiation dosages appear to result in copolymer samples giving approximately the same aged viscosities in the thermal aging tests. In general, these results indicate that the radiation initiated copolymers would be suitable for enhanced oil recovery operations under hostile environment conditions.

EXAMPLE XXXIV

Polymerization With Low Temperature Initiator

In this example the preparation of a series of 60/40 wt/wt N-vinyl-2-pyrrolidone/acrylamide copolymers at different solids level is described. The copolymerization was initiated by VAZO® 33 [2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile)] in the range of 0.05 to 0.10 phm.

The polymer samples were characterized by determining relative and inherent viscosities of polymer solutions (1000 ppm) in synthetic sea water at 25° C. The unaged viscosities of the polymer (2500 ppm) in synthetic sea water were determined by high pressure capillary viscometer at 250° F. Polymer solutions (2500 ppm) were aged for 7 days at 300° F before determining aged viscosities by high pressure capillary viscometry at 250° F. Results are summarized in the table below.

TABLE XLI

Aging Results on VAZO® 33 Initiated 60/40 Wt/Wt Copolymers of N-Vinyl-2-Pyrrolidone and Acrylamide in Synthetic North Sea Water (0.05 phm Initiator Level)				
% Total Solids	Relative Viscosity	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
			Unaged	Aged
1.0*	2.10	7.42	1.37	0.84
9.1	1.99	6.87	0.98	0.87
13.0	1.99	6.87	1.09	0.83
20.0	2.07	7.29	1.17	0.91
25.0	2.05	7.16	1.10	0.85
30.0	1.92	6.55	0.95	0.72
SNBW*	1.00	—	—	0.28

*SNBW represents synthetic North Sea water

*In this run VAZO® 33 was used at 0.1 phm.

Referring to the results in the above table, it can be seen that the VP/Am copolymers performed well in the thermal aging test exhibiting aged viscosities on the order of 2.5 to 3.5 times the viscosity of synthetic sea water at 250° F.

EXAMPLE XXXV

N-Vinyl-2-Pyrrolidone/N,N-Dimethylacrylamide/
Sodium 2-Acrylamido-2-Methylpropanesulfonate
Polymers

This example describes the preparation of polymers of NaAMPS, VP and DMAM using VAZO® 33 as the initiator (0.10 phm). Appropriate quantities of monomers were used to prepare NaAMPS/VP/DMAM polymers of the following compositions. 25/10/65 and 15/15/60. Reaction time was 24 hours at ambient temperature and the total solids level was 20%.

The gelled reaction masses were individually mixed with sufficient synthetic North Sea water to prepare 0.1 weight percent and 0.25 weight percent solutions for viscosity measurements. The results are summarized in Table XLII.

TABLE XLII

Aging Results on NaAMPS/VP/DMAM Polymers Aged in Synthetic North Sea Water			
Wt/Wt/Wt VP/DMAM/NaAMPS	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
		Unaged	Aged
25/10/65	6.70	1.24	1.05
25/15/60	6.88	1.28	0.95

Referring to the viscosity results in Table XLII, it is evident that the polymers would be useful as mobility buffers in hostile environments because the aged viscosities are about 3.3 to 3.8 times the viscosity of sea water at 250° F.

EXAMPLE XXXVI

VP/DMAM (50/50) and (40/60) Polymers and
VP/Am/DMAM Polymers

This example describes the preparation and testing of N-vinyl-2-pyrrolidone/N,N-dimethylacrylamide polymers and N-vinyl-2-pyrrolidone/acrylamide/N,N-dimethylacrylamide polymers. The copolymers were prepared in synthetic North Sea water, respectively, at 9.1% and 20% total solids, with 0.10 phm VAZO® 33 initiator. Two polymers 47.5/47.5/5 VP/Am/DMAM and 45/45/10 VP/Am/DMAM were similarly prepared and tested.

The gelled reaction masses were individually mixed with sufficient synthetic sea water to prepare 0.1 weight percent and 0.25 weight percent solutions for viscosity measurements. The results are summarized in Table XLIII.

TABLE XLIII

Aging Results on VP/DMAm Copolymers and VP/Am/DMAm Polymers Aged in Synthetic North Sea Water			
Wt/Wt/Wt VP/AM/DMAm	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
		Unaged	Aged
40/0/60	6.12	0.60	0.44
50/50/0	8.70	1.78	0.75
47.5/47.5/5	7.96	1.60	0.80
45/45/10	8.10	1.62	0.67
50/0/50	5.83	0.68	0.73

Referring to the results in Table XLIII, it can be seen that the compositions listed are suitable for use as mobility buffers in hostile environments because the aged viscosities are on the order of 2 to 3 times the viscosity of sea water at 250° F

EXAMPLE XXXVII

N,N-Dimethylacrylamide/Sodium
2-Acrylamido-2-Methylpropanesulfonate Copolymers

This example describes the preparation and testing of copolymers of DMAm and NaAMPS using VAZO @ 33 as the initiator (0.10 phm). The copolymerizations were carried out in distilled water at ambient temperatures for a period of 24 hours. The following DMAm/NaAMPS copolymers were prepared 60/40; 70/30; and 80/20

The gelled reaction masses were mixed individually with sufficient synthetic North Sea water to prepare 0.1 weight percent and 0.25 weight percent solutions for viscosity measurements. The results are summarized in Table XLIV

TABLE XLIV

Aging Results on DMAm/NaAMPS Copolymers Aged in Synthetic North Sea Water			
Wt/Wt DMAm/NaAMPS	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
		Unaged	Aged
40/60	8.48	2.08	0.86
30/70	7.85	2.07	1.37

The results in Table XLIV indicate that the DMAm/NaAMPS copolymers are potentially useful as mobility control agents in hostile environments because the aged viscosities of 3 to 5 times the viscosity of sea water at 250° F indicates excellent stability. In a related experiment, a 25/75 acrylamide/NaAMPS copolymer failed the thermal aging test (aged viscosity 0.33 cP). However, a 10/90 acrylamide/NaAMPS copolymer solution exhibited an aged viscosity of 0.53 cP which is about 2 times the viscosity of sea water at 250° F

EXAMPLE XXXVIII

VP/AM/NaAMPS Polymers

This example presents in tabular form (see Table XLV) a variety of VP/Am/NaAMPS polymer compositions which performed well enough in thermal aging tests to merit consideration as mobility control agents in hostile environments

TABLE XLV

Aging Results on Representative VP/Am/NaAMPS Polymers Aged in Synthetic North Sea Water			
Wt/Wt/Wt VP/Am/NaAMPS	Inherent Viscosity (dL/g)	Viscosity (cP) 250° F (2500 ppm)	
		Unaged	Aged
30/15/55	9.01	2.19	1.85
30/15/55	8.38	2.08	1.40
50/25/25	8.19	1.56	1.18
25/10/65	7.98	1.65	1.20
35/25/40	7.97	1.76	1.09
30/23/47	8.05	2.20	1.05
30/20/50	7.98	1.90	0.99
50/45/5	8.70	1.73	0.99
50/43/7	8.19	1.77	0.93
42.5/50/7.5	5.35	1.37	0.34

The last entry in Table XLV is a 42.5/50/7.5 VP/Am/NaAMPS polymer which performed very poorly in the thermal aging test (aged viscosity 0.34 cP, the viscosity of sea water at 250° F is about 0.28 cP). Part of this lack of thermal stability is believed related to the weight ratio of VP to Am in the polymer. Part is believed related to something which went wrong during the sample preparation. This polymer would be useful in lower temperature applications. It should be noted that in the first nine entries of Table XLV which all performed well in the thermal aging tests the polymers contained > 1:1 wt/wt ratio of VP:Am. The last polymer entry in the table contained < 1:1 wt/wt ratio of VP:Am

EXAMPLE XXXVIX

Potassium styrene Sulfonate/N,N-Dimethylacrylamide
Copolymer

This example describes the preparation and testing of a 30/70 weight percent potassium styrene sulfonate/N,N-dimethylacrylamide copolymer. The sample was prepared using practical grade potassium styrene sulfonate (4-vinyl benzene sulfonic acid potassium salt) available from Tridom Chemical Inc./Fluka A G. Copolymerization was carried out at 35% total solids in distilled water with VAZO @ 33 initiator at ambient temperature for a period of 24 hours.

The gelled reaction mass was mixed with sufficient synthetic North Sea water to prepare 0.1 weight percent and 0.25 weight percent solutions for viscosity measurements. An inherent viscosity of 3.44 dL/g and an aged viscosity of 0.77 cP were measured on the 0.1 weight percent and 0.25 weight percent solutions respectively

EXAMPLE XL

Inverse Emulsion Polymerization For Preparing
Hostile Environment Polymers

This example describes the preparation of poly(sodium 2-acrylamido-2-methylpropanesulfonate)(NaAMPS homopolymer), poly(N-vinyl-2-pyrrolidone)-sodium 2-acrylamido-2-methylpropanesulfonate(VP/NaAMPS copolymer) and poly(N-vinyl-2-pyrrolidone-co-acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate)(VP/Am/NaAMPS polymer) by inverse emulsion polymerization.

The recipes for the polymerizations are summarized in Table XLVI

TABLE XLVI

Recipes For Inverse Emulsion Polymerizations (Reaction Temperature 5° C., Reaction Time 120 Hours)								
Sample No.	Tetronic					50 Wt %		Wt/Wt/Wt
	Toluene (g)	H ₂ O (g)	1103 (g)	VP (g)	Am (g)	AQ-NaAMPS	VP/Am/NaAMPS	
1 ^a	40	20	5	9	4.5	33	30/15/55	
2 ^a	40	16.5	5	10	0	40	31/0/67	
3 ^a	40	6.5	0	0	0	60	0/0/100	

^aThe Initiator was VAZO @ 33 (0.30 phm) and the surfactant was a propargylated ethoxylated styrenesulfonate available from BASF Wyandotte under the trademark Tetronic 1103.

The above reaction charges were placed in individual 10 ounce crown top bottles to prepare, respectively, VP/Am/NaAMPS (30/15/55) polymer, VP/NaAMPS (33/67) polymer and NaAMPS homopolymer by inverse emulsion polymerization. The necessary amount of VAZO @ 33 was added as an aliquot of a stock solution of initiator in toluene. The surfactant was dissolved in toluene and added to the reactor bottle followed by the specified amounts of monomers and water. After degassing the reaction mixture for 20 minutes with argon, the bottle was capped and tumbled for about 5 days in a 5° C. constant temperature bath. The reaction products were milky fluids.

Portions of the milky fluids were individually mixed with sufficient synthetic North Sea water to give 0.1 wt % and 0.25 wt % solutions for viscosity measurements. The results are shown in Table XLVII.

TABLE XLVII

Aging Results in Synthetic North Sea Water With Polymers Prepared by Inverse Emulsion Polymerization				
Sample No.	Wt/Wt/Wt VP/Am/NaAMPS	Inherent Viscosity (dL/g)	Viscosity (cP) 250 F (2500 ppm)	
			Unaged	Aged
1	30/15/55	9.31	2.66	0.99
2	33/0/67	6.22	1.56	1.06
3	0/0/100	6.17	1.52	0.94

Referring to the results in Table XLVII, it is apparent that the disclosed polymers prepared by emulsion polymerization are potential candidates for mobility control agents in hostile environments because of their enhanced thermal stability indicated by the fact that their aged viscosities were on the order of 3 to 4 times the viscosity of seawater at 250 F.

FURTHER EXPERIMENTAL
EXAMPLE XLI

This example describes the preparation and thermal aging testing of two polymers prepared, respectively, by the copolymerization of N-methyl-N-vinyl acetamide (NMVA) with acrylamide (Am) and by the terpolymerization of NMVA with Am and sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS).

Appropriate quantities of monomers were used to prepare the NMVA/Am 50/50 wt/wt copolymer and the NMVA/Am/NaAMPS 30/15/55 wt/wt/wt terpolymer. The polymerizations were carried out in accordance with conventional solution polymerization technology using a total solids level of 30% in distilled water at ambient temperature with 0.1 phm of initiator.

The gelled reaction masses were mixed with sufficient synthetic North Sea water to prepare 0.1 weight percent and 0.25 weight percent solutions for solution viscosity measurements. The NMVA/Am 50/50 wt/wt copolymer solution exhibited an inherent viscosity of 11.1 dL/g and an aged solution viscosity of 1.3 centipoise. The NMVA/Am/NaAMPS 30/15/55 wt/wt/wt

terpolymer solution exhibited inherent viscosity of 9.6 dL/g and an aged solution viscosity of 1.7 centipoise. In Table XLVIII the performance of these polymers is compared to that of previously described hostile environment (HE) polymers VP/Am 50/50 wt/wt and VP/Am/NaAMPS 30/15/55.

TABLE XLVIII

N-Methyl-N-Vinyl Acetamide Derived Polymers For Use in Hostile Environments						
Run No.	Monomer Units (Wt %)				IV (0.10% SNSW 25° C.	Aged Viscosity/ SNSW (0.25)
	NMVA ^a	VP ^b	Am ^c	NaAMPS ^d		
1	50	0	50	0	11.1	1.3
2 ^a	0	50	50	0	8.9	1.2
3	30	0	15	55	9.6	1.7
4	0	30	15	55	8.5	1.7

^aA representative gel log sample of a 50/50 VP/Am copolymer was used in this test.
^bNMVA represents N-methyl-N-vinyl acetamide.
^cVP represents N-vinyl-2-pyrrolidone.
^dAm represents acrylamide.
^eNaAMPS represents sodium 2-acrylamido-2-methylpropanesulfonate.
^fIV represents inherent viscosity (dL/g) in Synthetic North Sea water.
^gAged viscosity is the observed solution viscosity after the solution was aged for one week at 300 F.

Referring to the aged solution viscosity results in runs 1 and 2 of Table XLVIII, it is evident that a solution of the 50/50 wt/wt NMVA/Am copolymer in SNSW exhibited a solution viscosity comparable to that of a solution of the 50/50 wt/wt VP/Am copolymer in SNSW. Perhaps this result reflects the comparable thermal stability of the NMVA/Am and VP/Am copolymers in SNSW solution. This behavior may be attributable to the capacity, respectively, of the NMVA and VP moieties to disproportionately retard the hydrolysis rate of the pendant acrylamide amide function. This is particularly remarkable since these compounds do not have the cyclic lactam structure which has been shown to enhance stability.

Referring to the aged solution viscosity results in runs 3 and 4 of Table XLVIII, it is evident that a solution of the 30/15/55 wt/wt/wt terpolymer in SNSW exhibited thermal stability comparable to that of a solution of the 30/15/55 wt/wt/wt VP/Am/NaAMPS terpolymer in SNSW. As indicated above, this result demonstrates the capacity of the NMVA and VP moieties to retard the hydrolysis rate of the pendant acrylamide amide function.

EXAMPLE XLII

This example described hostile environment polymers derived from methacrylate esters of hydroxylanesulfonic acids. This example is divided into three parts to cover (a) the homopolymer of 3-methacryloyloxypropanesulfonic acid and water soluble salts thereof (SPM), (b) copolymers of SPM with (i) N,N-dimethylacrylamide (DMAm), (ii) sodium 2-

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acrylamido-2-methylpropanesulfonate (NaAMPS), (iii) N-methylacrylamide (NMAm), (iv) N-(methacryloyloxyethyl)-N,N-dimethylaminopropanesulfonate betaine (SPED), (v) potassium 3-acryloyloxypropene-sulfonate (SPA) and (vi) N-vinyl-2-pyrrolidone (VP) and (c) terpolymers of SPM with (i) DMAm/NaAMPS, (ii) VP/Am and (iii) VP/NaAMPS.

All of the above polymers were prepared in accordance with conventional solution polymerization technology using total solids levels of 20-45% in distilled water at ambient temperature with about 0.1 phm of initiator. The cited weight percentages of polymer compositions reflects the relative weights of monomers charged to the polymerization zone.

(a) Homopolymers of SPM (potassium 3-methacryloyloxypropene sulfonate)

The gelled reaction masses form the homopolymerization runs were mixed with sufficient synthetic North Sea Water to prepare 0.1 weight percent and 0.25 weight percent solutions for solution viscosity measurements. Test results are summarized in Table XLIX

TABLE XLIX

SPM Homopolymer Performance in SNSW						
Run No.	% TS*	Units (Wt %)		IV (0.1) SNSW 25° C.	Viscosity 250 F (0.25 SNSW) cP	
		SPM ^a	SPA ^b		Unaged	Aged
1	30	100	0	7.4	1.8	1.6
2	35	100	0	8.3	1.9	1.5
3	45	100	0	8.6	2.3	1.8
4	30	0	100	8.5	3.1	Pynd ^g

*% TS represents % Total Solids in the polymerization medium.
^aSPM represents potassium 3-methacryloyloxy propenesulfonate.
^bSPA represents potassium 3-acryloyloxypropenesulfonate
^gSPA homopolymer system failed the thermal aging test (Precipitation).

Referring to runs 1, 2 and 3 in Table XLIX, it is evident that the SPM homopolymer in SNSW provided a solution which retained a significant percentage of its viscosity after thermal aging and the average solution viscosity of the thermally aged solution was 5.7 times that of sea water at 250 F. This behavior indicates that SPM homopolymer is potentially useful in mobility control under hostile environment conditions.

Attention is called to the unexpected result observed in run 4 of Table XLIX. The homopolymer of SPA (the lower homolog of SPM) failed to impart thermally stable viscosity to the solution in the high temperature test precipitation accompanied the loss of solution viscosity

(b) Copolymers of SPM
(i) DMAm/SPM (wt/wt) 10/90, 20/80, 30/70, 40/60, 50/50, 65/35/ 80/20

TABLE L

Performance Test Results on DMAm/SPM Copolymers*					
Run No.	Monomer Units (Wt %)		IV (0.1) SNSW 25° C.	Viscosity 250 F (0.25 SNSW) cP	
	DMAm ^a	SPM ^b		Unaged	Aged
C	100	0	NM ^g	0.76	0.44
4	10	90 ^c	7.2	3.0	2.3
5	20	80	8.0	3.2	2.2
6	30	70	8.0	3.5	2.4
7	40	60	8.3	3.7	2.5
8	50	50	8.8	3.4	2.5
9	65	35	8.8	2.8	1.3
10	80	20	8.9	1.8	0.9

*Copolymers in runs 4-10 were prepared at 30% Total Solids.
^aDMAm represents N,N-dimethylacrylamide.
^bSPM represents potassium 3-methacryloyloxypropenesulfonate.
^cThis copolymer was prepared at 30% Total Solids. Another sample prepared at 40% Total Solids gave an aged viscosity of 2.9 cP
^gNM represents Not Measured.

Referring to the results in Table L, it is evident that copolymers of DMAm and SPM, especially those compositions containing 50 or more weight percent SPM are good candidates for mobility control under hostile environment conditions the average aged solution viscosity, e.g., in runs 4-8 being 8.5 times the viscosity of sea water at 250 F. The homopolymer (see run C) of DMAm in SNSW exhibited an aged solution viscosity which was only about 1.6 times the aged viscosity of sea water at 250 F

(ii) NaAMPS/SPM (wt/wt) 10/90, 15/85, 25/75, 30/70, 50/50, 65/35

TABLE L

Performance Test Results on NaAMPS/SPM Copolymers*					
Run No.	Monomer Units (Wt %)		IV (0.1) SNSW 25° C.	Viscosity 250 F ** (0.25 SNSW) cP	
	NaAMPS ^a	SPM ^b		Unaged	Aged
11	10	90 ^c	6.7	2.1	1.9
12	15	85	6.4	1.9	1.8
13	25	75	6.2	1.8	1.6
14	30	70	6.5	1.6	0.7
15	50	50	6.1	1.1	1.1
16	65	35	5.3	1.2	1.1

*Copolymers in runs 11-16 were prepared at 30% Total Solids.
^aNaAMPS represents sodium 2-acrylamido-2-methylpropanesulfonate.
^bSPM represents potassium 3-methacryloyloxypropenesulfonate
^cThis copolymer was prepared at 30% Total Solids. Another sample prepared at 15% Total Solids gave an aged solution viscosity of 1.7 cP
^{**}Viscosity of sea water at 250 F is about 0.25 cP

Referring to the result in Table LI, it is evident that copolymers of NaAMPS and SPM over a range of compositions are good candidates for mobility control under hostile environment conditions. the average aged viscosity being about 4.9 times the viscosity of sea water at 250 F

(iii) NMAm/SPM (wt/wt) 10/90
(iv) SPED/SPM (wt/wt) 30/70
(v) SPA/SPM (wt/wt) 30/70
(vi) VP/SPM (wt/wt) 20/80, 10/90

TABLE LI

Performance Test Results on NMAm/SPM SPED/SPM, SPA/SPM and VP/SPM Copolymers*									
Run No.	Monomer Units (Wt %)					IV (0.1) SNSW 25° C.	Viscosity 250 F (0.25 SNSW) cP		
	NMAm ^a	SPED ^b	SPA ^c	SPM ^d	VP ^e		Unaged	Aged	
17	10	0	0	90	0	6.5	1.6	0.9	
18	0	30	0	70	0	7.4	2.4	1.2	
19	0	0	30	70	0	6.7	1.6	1.1	
20	0	0	0	80	20	6.5	1.6	0.9	

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TABLE LII-continued

Performance Test Results on NMAm/SPM
SPED/SPM, SPA/SPM and VP/SPM Copolymers^a

Run No.	Monomer Units (Wt %)						Viscosity 250 F (0.25 SNSW) cP	
	NMAm ^a	SPED ^b	SPA ^c	SPM ^d	VP ^e	IV (0.1) SNSW 25 C	Unaged	Aged
21	0	0	0	90	10	7.5	1.6	1.3

^aCopolymers in runs 17-19 were prepared at 30% Total Solids.

^bNMAm represents N-methylacrylamide.

^cSPED represents N-(methacryloyloxyethyl)-N,N-dimethylaminepropanesulfonate betaine.

^dSPA represents potassium 3-acryloyloxypropylsulfonate.

^eSPM represents potassium 3-methacryloyloxypropylsulfonate.

^fVP represents N-vinyl-2-pyrrolidone.

Referring to the results in Table LII, it is evident that the various copolymers of SPM are potentially useful in hostile environments because the aged solution viscosities were 3.2 to 4.6 times the viscosity of sea water at 250 F. It is noteworthy that in spite of the fact that the SPM homopolymer is effective a 10/90 Am/SPM copolymer is SNSW on aging at 250 F was not effective as evidenced by an aged solution viscosity of 0.3 cP which is essentially the same as the viscosity of SNSW at 250 F.

(c) Terpolymers of SPM

(i) DMAm/NaAMPS/SPM (wt/wt) 80/10/10, 60/20/20, 30/30/40, 20/60/20, 15/15/70

TABLE LIII

Performance Test Results on
DMAm/NaAMPS/SPM Terpolymers^a

Run No.	Monomer Units (Wt %)				IV (0.1) SNSW 25 C	Viscosity 250 F (0.25 SNSW) cP	
	DMAm ^a	NaAMPS ^b	SPM ^c	25 C		Unaged	Aged
22	80	10	10	9.2	2.1	0.7	
23	60	20	20	8.8	3.2	1.5	
24	30	40	30	7.7	2.7	1.6	
25	20	20	60	8.2	3.2	2.0	
26	15	70	15	6.8	1.7	1.3	

^aTerpolymers were prepared at 30% Total Solids.

^bDMAm represents N,N-dimethylacrylamide.

^cNaAMPS represents sodium 2-acrylamido-2-methylpropanesulfonate.

^dSPM represents potassium 3-methacryloyloxypropylsulfonate.

Referring to the results in Table LIII, it is evident that the various terpolymers of SPM are potentially useful in hostile environments because the aged solution viscosities were 2.5 to 7 times the viscosity of sea water at 250 F.

(ii) VP/Am/SPM (wt/wt) 50/30/20, 30/10/60, 40/15/45, 40/30/30

(iii) VP/NaAMPS/SPM (wt/wt) 20/60/20

TABLE LIV

Performance Test Results on VP/Am/SPM and
VP/NaAMPS/SPM Terpolymers^a

Run No.	Monomer Units (Wt %)				IV (0.1) SNSW 25 C	Viscosity 250 F (0.25 SNSW) cP	
	VP ^a	Am ^b	NaAMPS ^c	SPM ^d		Unaged	Aged
27	50	30	0	20	7.1	1.3	0.7
28	30	10	0	60	7.5	2.5	0.7
29	40	15	0	45	7.2	1.5	0.6
30	40	30	0	30	8.3	1.3	0.5

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TABLE LIV-continued

Performance Test Results on VP/Am/SPM and
VP/NaAMPS/SPM Terpolymers^a

Run No.	Monomer Units (Wt %)				IV (0.1) SNSW 25 C	Viscosity 250 F (0.25 SNSW) cP	
	VP ^a	Am ^b	NaAMPS ^c	SPM ^d		Unaged	Aged
31	20	0	60	20	7.2	1.6	1.3

^aTerpolymers in runs 28-31 were prepared at 30% Total Solids.

^bVP represents N-vinyl-2-pyrrolidone.

^cAm represents acrylamide.

^dNaAMPS represents sodium 2-acrylamido-2-methylpropanesulfonate.

^eSPM represents potassium 3-methacryloyloxypropylsulfonate.

Referring to the results in Table LIV, it is evident that the various terpolymers of SPM are potentially useful in hostile environments because the aged solution viscosities were about 1.8 to 4.6 times the viscosity of sea water at 250 F. Referring to run 31 in Table LIV, it can be concluded that the 20/60/20 VP/NaAMPS/SPM terpolymer (see aged solution viscosity) performed better than the VP/Am/SPM terpolymers of runs 27-30.

EXAMPLE XLIII

This example describes the use of selected hostile environment polymers as high temperature high pressure water loss control agents in drilling muds. The following polymers were tested as water loss control agents:

(a) Poly(N-vinyl-2-pyrrolidone-co-sodium 2-acrylamido-2-methylpropanesulfonate) (VP/NaAMPS) (20/90 wt/wt)

(b) Poly(N-vinyl-2-pyrrolidone-co-acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate) (VP/Am/NaAMPS) (30/15/55 wt/wt/wt)

(c) Poly(N-vinyl-2-pyrrolidone-co-acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate-co-sodium acrylate) (VP/AM/NaAMPS/NaAA)

Polymer samples received as gel logs were diluted to four percent solutions to assure good dispersion in muds. The high solids muds were cooled to ambient temperature and allowed to stand for 2 hours before any tests were carried out. Plastic viscosity (PV), yield point (YP), gel strength (Gels) and water loss at room temperature (RTWL mL/30 min) were determined in accordance with API RP 13B.

After the initial tests, the mud samples were aged at a specified temperature for 16 hours before repeating the above tests. The most severe test carried out on the muds was a water loss test at 325 F and 500 psi (HTWL, High Temperature Water Loss).

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TABLE LV

Hostile Environment Polymers To Control Water Loss in 12.2 lb/gal Saltwater Mud* (2 lb/bbl polymer)										
Polymer Additive	Run No.	Initial Properties				Final Properties (aged 16 Hrs @ 360 F.)				
		PV ^a /YP ^b	Gels ^c	pH	WL ^d	PV ^a /YP ^b	Gels ^c	pH	WL ^d	HTWL ^e
VP/NaAmPS (10/90)	1	32/36	25/65	9.7	4.0	29/33	22/33	7.3	6.1	22.0
VP/Am/NaAMPS (30/15/55)	2	19/13	7/56	10.1	NM ^f	21/33	12/78	7.4	6.5	29.0
VP/Am/NaAMPS/NaAA (20/10/55/3)	3	20/30	38/95	10.1	3.6	23/37	23/98	7.4	5.6	27.0

^fNM represents Not Measured.
^aPV represents Plastic Viscosity centipoise.
^bYP represents Yield Point, lb/100 ft².
^cGels represents Gel Strength, 10 sec/10 min, lb/100 ft².
^dWL represents Water Loss (mL/30 min, @ ambient temperature).
^eHTWL represents High Temperature Water Loss (mL/30 min; @ 325 F and 500 psi). The thermally aged sample (16 hrs @ 360 F.) was cooled to ambient temperature and Water Loss was determined at room temperature (see values under WL on right hand side of Table VII). A thermally aged sample was then taken to 325 F and 500 psi to determine the HTWL values.
^fSaltwater used contained 1.7 percent bentonite, 9.15 percent P95 illite clay and 30 percent barite in 4 percent salt water. An additional 10 lb/bbl NaCl was added after treatment with 5 lb/bbl Tannathin lignite, 3 lb/bbl Desco @ thinner NaOH and polymer.

Referring to the water loss values in Table LV, it is evident that the mud system of run 1 containing the 10/90 VP/NaAMPS copolymer additive was somewhat more effective than the polymer additives of runs 2 and 3 for controlling water loss particularly at high temperature.

EXAMPLE XLIV

This example compares the performance of poly(N-vinyl-2-pyrrolidone-co-sodium 2-acrylamido-2-methylpropanesulfonate) (VP/NaAMPS) (10/90 wt/wt) in drilling muds with the performance of several commercially available drilling mud additives.

The tests were carried out in 12.2 lb/gal saltwater muds. The base mud contained 2.7 percent bentonite, 9.15 percent P95 illite clay and 30 percent barite in 4 percent salt water. An additional 20 lb/bbl salt was added after treatment with 5 lb/bbl Tannathin lignite, 2 lb/bbl Desco @ thinner, NaOH and polymer. The tests were carried out as described in the previous example. Results are summarized in Table LVI.

TABLE LVI

Comparison of 10/90 VP/NaAMPS HTWL Additive With Commercial Additives (2 lb/bbl Additive)										
Additive	Run No.	Initial Properties				Final Properties (aged 16 Hrs @ 360 F.)				
		PV ^a /YP ^b	Gels ^c	pH	WL ^d	PV ^a /YP ^b	Gels ^c	pH	WL ^d	HTWL ^e
10/90 VP/NaAMPS	1	29/36	18/53	10.2	4.7	27/31	20/38	7.4	6.1	26.0
Base Mud	2	10/13	12/33	10.4	27.0	9/20	14/19	7.7	46.0	NM ^f
Milchem Kem Seal	3	21/22	13/48	10.5	5.9	21/22	5/30	7.5	7.7	36.0
Barcol Therman-Chok	4	13/6	2/12	10.2	7.1	12/13	3/13	7.3	18.5	80.0
Imco Densol	5	12/8	1/8	9.8	7.0	13/9	2/11	7.2	16.3	78.0
Nat'l Starch Versa TL 600	6	11/16	13/48	10.2	11.6	13/21	22/40	7.6	16.9	35.0
Henkel Rheothick 80-11	7	19/22	16/36	10.2	18.4	22/20	2/5	7.4	6.2	25.0
Hoechst Hoesadrill 2825	8	15/6	1/8	9.9	5.7	13/7	2/9	7.1	13.7	70.0
Hoesadrill V3118	9	14/3	1/7	9.7	7.0	15/8	1/8	7.0	9.6	46.0

^fNM represents Not Measured.
^aSee footnotes a, b, c, d and e in Example XLIII (Table LV).

Referring to the results in Table LVI, it is evident that the 10/90 VP/NaAMPS copolymer additive in run 1 imparted better water loss control properties both at ambient temperature (WL values) and at elevated temperature (HTWL values) than did the commercially available additives of runs 3, 4, 5, 6, 8 and 9. The commercial additive in run 7 proved to be comparable in performance to the 10/90 VP/NaAMPS copolymer.

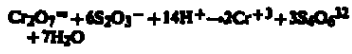
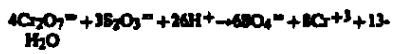
EXAMPLE XLV

This example describes the modification of VP and/or AMPS copolymers or terpolymers with acrylic acid in order to incorporate sufficient carboxylic acid groups in the polymer structure so that gelation of these poly-

mers, i.e., crosslinking of these polymers with polyvalent metal cations such as Cr(III), is facilitated. Incorporation of the acrylic acid units into the polymer is preferably carried out by copolymerizing acrylic acid with the appropriate monomers to produce "acrylic acid modified" polymers such as e.g., poly(N-vinyl-2-pyrrolidone-co-acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate-co-acrylic acid) (30/10/55/5) (VP/Am/NaAMPS/AA) and poly(N-vinyl-2-pyrrolidone-co-acrylamide-co-acrylic acid) (50/45/5) (VP/Am/AA).

These acrylic acid modified polymers were prepared in accordance with conventional solution polymerization technology using total solids levels of 20-30% in distilled water at ambient temperature with about 0.1 phm of initiator. The cited weight percentages in the polymer compositions reflect the relative weights of monomers charged to the polymerization zone, e.g., the 50/45/5 VP/Am/AA polymer was prepared by charging, respectively, 50, 45 and 5 parts by weight of VP, Am and AA to the polymerization zone.

The dichromate-thiosulfate redox couple was used in the laboratory experiments to demonstrate the gelation of the acrylic acid modified polymers. The Cr(III) crosslinking agent is generated from the redox couple as indicated by either of the equations



The polyvalent metal cation crosslinking agent presumably coordinates with the pendant carboxylic acid

groups It is contemplated that acrylic acid modified polymers can be gelled with other conventional cross-linking agents such as, e.g., chromium(III) propionate, aluminum citrate, chromium(III) acetate, chromium(III) citrate and the like as well as other known redox couples such as dichromate-bisulfite and the like.

In the experimental test runs, stock solutions of dichromate, thiosulfate and acrylic acid modified polymer were used to charge the respective components to the gelation vessel. In order to maintain anaerobic test conditions, capped 10 ounce pop bottles were used as gelation vessels. Three hole metal caps with rubber seals provided a means for injecting reagents into the vessel and withdrawing samples from the vessel with syringes thereby minimizing contact of the system with oxygen. Laboratory manipulations were routinely carried out in a glove box with an inert gas atmosphere such as helium or nitrogen to further minimize the possibility of contact with oxygen. The pop bottles containing the aqueous test mixtures of polymer, dichromate and thiosulfate were incubated at a specified temperature such as 120 F. At specified time intervals, pop bottles were removed from the constant temperature or incubation zone and examined for the extent of gelation before returning the vessel for further incubation.

As the work progressed, it was established that procedures could be done at the lab bench provided that all systems were purged with an inert gas before capping the bottles and all transfers of materials were made by syringe.

Gels were qualitatively evaluated by noting the tendency of the gels to flow as reflected by tongue length measurements. Zero on the tongue length scale being defined by the fluid level in the bottle when the bottle is in the upright position. Initial tongue length measurements were taken to the nearest sixteenth of an inch with the bottle in a horizontal position. If the gel fluid touched the inside of the bottle cap with the bottle in a horizontal position, the fluid was considered not gelled (NG). In the horizontal position, tongue lengths of 4 to 5 inches were considered light to very light gels. These are gel systems that still flowed quite readily but the "gel tongue" did not contact the cap when the bottle was in the horizontal position. As gelation progressed, the measured tongue length became shorter.

As the gel assumed a firmer character, the bottle was tilted downward 15° from the horizontal before measuring the tongue length. Tongue lengths of 0 to 2 inches were considered hard gels, tongue lengths of 2 to 4 inches were considered medium gels, and tongue lengths of 4 to 5½ inches were considered light gels.

The dichromate stock solution was prepared by dissolving 20 grams of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ in sufficient water to give 100 mL of stock solution. The polymer stock solution was prepared by dissolving sufficient polymer in water to give a 1 weight percent solution of polymer (active basis). The thiosulfate stock solution was prepared by dissolving 50 grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in sufficient water to give 100 mL of solution.

One hundred gram portions of the polymer solution were usually used in the test runs. A test level of 600 ppm $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ required the addition of 0.3 mL of the dichromate stock solution. A sufficient amount of the thiosulfate stock solution was added to the system so that the ppm ratio of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ to $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ was on the order of 5:1, viz., about 3000 ppm reductant to 600 ppm oxidant. Synthetic Arkansas-Burbank river water was used in the preparations of all the experimental solutions. In many runs, the dichromate level was increased to 1200 ppm and the thiosulfate level was increased to 6000 ppm.

Representative gel test results are summarized in Tables LVII and LVIII.

Referring to the results in Table LVII, it is evident that the unmodified VP/Am (50/50) polymer failed to gel in the fresh water medium at 120 F (run 1). Apparently this was due to the lack of carboxyl groups in the polymer.

Referring to runs 2 through 5, it is evident that the polymers gelled apparently due to the presence of pendant carboxylic acid groups on the acrylic acid units. In run 3, the concentration of dichromate and thiosulfate were doubled relative to the concentrations used in run 2 resulting in the formation of hard gel in a short time (1 day) at the higher concentration. The VP/Am/AA (50/45/5) system (run 4) produced a hard gel (H) in 2 days whereas the VP/Am/AA (50/40/10) system (run 5) required 8 days for the formation of a hard gel.

Referring to the results in Table LVIII, it is evident that the unmodified VP/Am/NaAMPS (30/15/55) polymer failed to gel in the fresh water medium at 120 F (run 6). Presumably this was due to the lack of carboxyl groups in the polymer. Referring to runs 7-11, it is evident that polymers bearing the carboxylic acid groups on the acrylic acid units were gelable under the conditions of the test. Runs 9 and 11 (compared to 8 and 10) indicate that gelation was more extensive if the dichromate and thiosulfate concentrations were doubled. Referring to runs 10 and 11, it appears that polymers with higher levels of acrylic acid are less readily gelled. Higher concentration levels of the redox components may be necessary at the higher acrylic acid loadings. Presently, it is preferred that the acrylic acid monomer level be in the range of 1 to 15 weight percent.

TABLE LVII

Gelation* Studies On Acrylic Acid Modified VP ^a /Am ^b Polymer (Fresh Water 120 F)		Character of Gel ^d																	
		Period of Days																	
Polymer	Run No.	<1	1	2	3	4	8	14	16	22	23	27	31	34	42	50	65		
VP ^a /Am ^b (50/50)	1	L	L	L	L		L	L				L	L						
VP/Am/AA (50/49/1)	2	L	M	M	M	M	M		M	M				M		M			
VP/Am/AA (50/49/1)†	3	L	H	H	H	H	H		H	H				H		H			
VP/Am/AA (50/45/5)	4		M	H	H	H	H		H	H				H		H			

TABLE LVII-continued

Gelation* Studies On Acrylic Acid Modified VP ^a /Am ^b Polymer (Fresh Water 120 F)															
Polymer	Run No.	Character of Gel ^d Period of Days													
		<1	1	2	3	4	8	14	16	22	23	27	31	34	42

VP/Am/AA (30/40/10) 3 L L M H H H H H H H

*The redox couple of sodium dichromate (oxidant) and sodium thiosulfate (reductant) was used as the gelling system (600 ppm oxidant, 2850 ppm reductant).
#In this run 1250 ppm oxidant and 5740 ppm reductant was used.
^aVP represents N-vinyl-2-pyrrolidone.
^bAm represents acrylamide
^cAA represents acrylic acid.
^dGels are characterized as hard (H), medium (M) and light (L). The tongue length ranges for these designations are, respectively 0 to 2 inches, 2 to 4 inches and 4 to 5 1/2 inches in a 10 ounce bottle tilted downward 15° below horizontal. In the horizontal position, tongue lengths of 3 to 5 1/2 inches are designated as light (L) gels. Firm gels which peeled away from the walls of the pop bottle but otherwise maintained their integrity during the test were still counted as H gels.

TABLE LVIII

Gelation* Studies On Acrylic Acid Modified VP ^a /Am ^b /NaAMPS ^c /AA ^d terpolymer (Fresh Water 120 F)																		
Polymer	Run No.	Character of Gel ^d Period of Days																
		<1	1	2	3	4	8	14	16	22	23	27	31	34	42	90	128	

VP/Am/NaAMPS (30/15/35) 6 L L L L L L L L L L L L L L L L L
VP/Am/NaAMPS/AA (30/14/55/1) 7 L L L L L L L L L L L L L L L L L
VP/Am/NaAMPS/AA (30/10/55/5) 8 L L L L L L L L L L L L L L L L L
VP/Am/NaAMPS/AA# (30/10/55/5) 9 L M H H H H H H H H H H H H H H
VP/Am/NaAMPS/AA (30/5/55/10) 10 NG[‡] NG NG NG NG NG NG NG NG NG NG NG NG NG NG NG
VP/Am/NaAMPS/AA# (30/5/55/10) 11 NG NG NG NG NG L L M H[¶]

*See * footnote in Table LVII
#See # footnote in Table LVII
^aSee footnotes a and b in Table LVII.
^bNaAMPS represents sodium 2-acrylamido-2-methylpropanesulfonate.
^cSee footnote c in Table LVII
^dAA represents acrylic acid.
^eSeven days.
^fTwelve days: Hard gel (H) had peeled from walls of bottle but the gel exhibited no symmetry.
[‡]Seventy-four days. Same condition as footnote g.
[§]NO represents not gelled. Fluid flowed to bottle cap in horizontal orientation of the bottle.
[¶]Fifty-three days.

EXAMPLE XLVI

This example describes the modification of polymers with sodium acrylate in order to incorporate sufficient carboxylate groups in the polymer structure so that gelation of these polymers, i.e., crosslinking of these polymers with polyvalent metal cations such as Cr(III), is facilitated. Incorporation of the sodium acrylate units into the polymer is preferably carried out by copolymerizing sodium acrylate with the appropriate monomers to produce "sodium acrylate modified" polymers such as e.g., poly(N-vinyl-2-pyrrolidone-co-acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate-co-sodium acrylate) (30/10/55/5) (VP/Am/NaAMPS/NaAA) and poly(N-vinyl-2-pyrrolidone-co-acrylamide-co-sodium acrylate) (590/45/5) VP/Am/NaAA, and poly(N-vinyl-2-pyrrolidone-co-sodium 2-acrylamido-2-methylpropanesulfonate-co-sodium acrylate)(VP/NaAMPS/NaAA)(30/30/10).

These sodium acrylate modified polymers were prepared in accordance with conventional solution polymerization technology using total solids levels of 20-20% in distilled water at ambient temperature with about 0.1 phm initiator. The cited weight percentages in the polymer compositions reflect the relative weights of monomers charged to the polymerization zone, e.g., the 50/45/5 VP/Am/NaAA polymer was prepared by charging, respectively, 50, 45 and 5 parts by weight of VP, Am and NaAA to the polymerization zone. It was highly preferred to use aliquots of a 25 weight percent aqueous solution of sodium acrylate for introducing the desired amount of NaAA. Alternatively, the proper relative amounts of VP, Am and acrylic acid could be charged to the polymerization zone and the pH adjusted to convert the acrylic acid to sodium acrylate prior to the polymerization. The experimental procedures described in Example XLV were used in this example to prepare and evaluate the gels derived from sodium acrylate modified polymers. Results are summarized in Tables LIX and LX.

TABLE LIX

Gelation* Studies On Sodium Acrylate Modified VP ^a /Am ^b Polymer (Fresh Water 200 F)																		
Polymer	Run No.	Character of Gel ^d Period of Days																
		<1	1	2	5	6	8	11	14	16	21	24	29	41	42	47	71	

VP/Am (30/30) 12 NG[§]
VP/Am/NaAA^c (30/49/1) 13 H H H H H H H H H H H H H H H H
VP/Am/NaAA (30/40/10) 14 H H H H H H H H H H H H H H H H
VP/Am/NaAA (30/30/20) 15 L M H H H H H H H H H H H H H H

TABLE LIX-continued

Gelation ^a Studies On Sodium Acrylate Modified VP ^a /Am ^b Polymer (Fresh Water 200 F)															
Polymer	Run No.	Character of Gel ^d Period of Days													
		<1	1	2	5	6	8	11	14	16	21	24	29	41	42

VP/Am/NaAA (30/10/40)	16	NG ^e	NG	NG				H		H		H			H
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^aThe redox couple of sodium dichromate (oxidant) and sodium thiosulfate (reductant) was used as the gelling system (1200 ppm oxidant, 6000 ppm reductant).
^bSee footnotes a and b in Example XLV (Table LVII).
^cNaAA represents sodium acrylate.
^dSee footnote d in Example XLV (Table LVII).
^eNG represents Not Gelled; fluid flowed to bottle cap when bottle was positioned in a horizontal orientation.
^fNot gelled (NG) after 14 days in fresh water @ 200 F, not gelled (NG) after 14 days in Synthetic North Sea water @ 200 F

TABLE LX

Gelation ^a Studies On Sodium Acrylate Modified VP ^a /Am ^b /NaAMPS ^c /AA ^d terpolymer (Fresh Water 200 F)															
Polymer	Run No.	Character of Gel ^d Period of Days													
		<1	1	2	4	5	9	18	25	35	38	61	64	71	93

VP/Am/NaAMPS (30/15/55)	18						NG ^f								
VP/Am/SA ^g /NaAA (30/10/35/5)	19	M	H	H	H			M		M				M	M
VP/Am/SA/NaAA (30/10/30/10)	20	M	H	H	H		H	H		M		M		M	
VP/Am/SA/NaAA (30/10/40/20)	21	NG ^f	NO			H			H	H		H		H	
VP/SA/NaAA (30/60/10)	22 ^h	L		H					H ⁱ						H ^j

^aThe redox couple of sodium dichromate (oxidant) and sodium thiosulfate (reductant) was used as the gelling system (1200 ppm oxidant, 6000 ppm reductant).
^bSee footnotes a and b in Example XLV (Table LVII).
^cSA and NaAMPS represent sodium 2-acrylamido-2-methylpropanesulfonate.
^dSee footnote d in Example XLV (Table LVII).
^eNaAA represents sodium acrylate.
^fNG represents Not Gelled; fluid flowed to bottle cap when bottle was positioned in a horizontal orientation.
^gNot gelled (NG) after 11 days in fresh water @ 200 F, not gelled (NG) after 11 days in Synthetic North Sea water @ 200 F
^hGelatin medium was Synthetic North Sea water @ 200 F
ⁱTime period was 24 days.
^jTime period was 167 days.

It was noteworthy that the shelf-life of the sodium acrylate modified polymers was significantly longer than the shelf life of the acrylic acid modified polymers described in Example XLV. This was reflected by the loss of water solubility in the acrylic acid modified polymers. This behavior is presumably due to the acid promoted imidization of pendant —CONH₂ groups wherein the pendant —CO₂H groups of the acrylic acid units are sufficiently acidic to promote the imidization. Since the sodium acrylate modified polymers lacked pendant —CO₂H groups, no built-in acidic promoter was present to trigger the imidization reaction between pendant —CONH₂ groups. Of the modified polymers, the sodium acrylate modified compositions are presently preferred over the analogous acrylic acid modified compositions.

Referring to the results in Table LIX, it is evident that the unmodified VP/Am (30/50) polymer failed to gel in either the fresh water medium at 200 F (run 12) or in the synthetic North Sea water medium at 200 F (footnote f). Presumably this was due to the absence of carboxylate groups in the polymer. Referring to the results in runs 13 through 16, it is evident that the sodium acrylate modified polymers were gelable under the test conditions. The slower gelation rate observed in run 16 may be due to the relatively high level of sodium acrylate in the polymer, i.e., 40 weight percent. Once again the gelation capacity of the various polymers was probably due to the presence of carboxylate groups pendant from the sodium acrylate units.

Referring to the results in Table LX, it is evident that the unmodified VP/Am/NaAMPS (30/15/55) polymer failed to gel in either the fresh water medium at 200 F (run 18) or in the Synthetic North Sea water medium at 200 F (footnote g). Apparently this was due to the absence of carboxylate groups in the polymer. Refer-

ring to the results in runs 19 through 21, it is evident that the sodium acrylate modified polymers were gelable under the test conditions. In run 22, a sodium acrylate modified polymer was gelled in Synthetic North Sea water at 200 F. The slower gelation rate noted in run 21 may have been due to the relatively higher level of sodium acrylate, i.e., 20 weight percent. Even higher levels of the redox components may be necessary to gel polymers with higher carboxylate loadings. Presently, it is preferred that the carboxylate monomer level be in the range of 1 to 15 weight percent.

EXAMPLE XLVII

This example describes the preparation of magnesium 2-acrylamido-2-methylpropanesulfonate 4-hydrate [Mg(AMPS)₂·4H₂O] from the reaction of magnesium acetate 4-hydrate [Mg(OAc)₂·4H₂O] with either (a) refined grade 2-acrylamido-2-methylpropanesulfonic acid (AMPS) or (b) commercial grade AMPS.

Thermal aging test data are also presented in this example for (i) poly(magnesium 2-acrylamido-2-methylpropanesulfonate), (ii) poly(magnesium 2-acrylamido-2-methylpropanesulfonate-co-sodium 2-acrylamido-2-methylpropanesulfonate) (30/50 wt/wt) [Mg(AMPS)₂/Na(AMPS)], and (iii) poly(magnesium 2-acrylamido-2-methylpropanesulfonate-co-sodium 2-acrylamido-2-methylpropanesulfonate) (10/90 wt/wt) [Mg(AMPS)₂/Na(AMPS)]. The cited weight percentages of monomers in these polymer compositions reflects the relative weights of monomers charged to the polymerization zone, e.g., for the 50/50 wt/wt [Mg(AMPS)₂/Na(AMPS)] polymer, equal weights of magnesium 2-acrylamido-2-methylpropanesulfonate

and sodium 2-acrylamido-2-methylpropanesulfonate were charged to the polymerization zone

(a) Preparation of $Mg(AMPS)_2 \cdot 4H_2O$ from refined grade AMPS.

In a glass reactor equipped with an inlet tube for purging the system continuously with air was placed 60 g distilled water and 26.6 g (0.12 mole) of magnesium acetate 4-hydrate. This solution was stirred and maintained under air blanket as 50 g (0.24 mole) of refined grade 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was slowly added and the reaction mixture temperature was kept below 30° C.

After addition of the refined grade AMPS, the entire reaction mass was poured into a 3 l volume/volume mixture of acetone (1500 mL) and cyclohexane (500 mL) to precipitate magnesium 2-acrylamido-2-methylpropanesulfonate 4-hydrate, $Mg(AMPS)_2 \cdot 4H_2O$ (FWt 508). This mixture was chilled in an ice bath for one hour before removing the precipitate by suction filtration. The product was washed twice with 100 mL portions of cyclohexane and dried in vacuo at ambient temperature to give approximately a quantitative yield of $Mg(AMPS)_2 \cdot 4H_2O$.

(b) Preparation of $Mg(AMPS)_2 \cdot 4H_2O$ from commercial grade AMPS.

In a glass reactor equipped with an inlet tube for purging the system continuously with air was placed 80 g distilled water and 39.5 g (0.18 mole) of magnesium acetate 4-hydrate. This solution was stirred and maintained under air as 78 g (0.36 mole active basis) of commercial grade 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was slowly added and the reaction mixture temperature was kept below 30° C. The reaction mixture was stirred an additional 15 minutes after all the AMPS had been added. In order to solubilize all the components in the mixture, the stirred mixture was allowed to warm to ambient temperature.

The entire reaction mass was poured into a 5 l volume/volume mixture of acetone (2500 mL) and cyclohexane (500 mL) to precipitate $Mg(AMPS)_2 \cdot 4H_2O$. This mixture was chilled in an ice bath for one hour before removing the precipitate by suction filtration. The product was washed three times with 100 mL portions of cyclohexane and dried in vacuo at 40° C. to give about a 95% yield of $Mg(AMPS)_2 \cdot 4H_2O$.

The polymers used in the thermal aging tests were prepared in accordance with conventional solution polymerization technology using total solids levels of 20-30% in distilled water at ambient temperature with about 0.1 phm of initiator. The samples of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and $Mg(AMPS)_2 \cdot 4H_2O$ used in the polymerizations were prepared from refined grade AMPS. The gelled reaction masses from the polymerizations were mixed with sufficient synthetic North Sea water to prepare 0.1 weight percent and 0.25 weight percent solutions for solution viscosity measurements. Test results are summarized in Table LXI.

TABLE LXI

Mg(AMPS) ₂ Polymer in Synthetic North Sea Water (SNSW)					
Run No.	Monomer Units (Wt %)		IV (0.1) SNSW	Viscosity 250 F (0.25 SNSW) cP	
	Mg(AMPS) ₂	NaAMPS	25° C.	Unaged	Aged
1	100	0	9.99	2.42	1.76
2	50	50	9.89	2.71	1.97
3	10	90	8.65	2.18	1.73

Referring to the results in Table LXI, it is evident that the $Mg(AMPS)_2$ -containing polymers in SNSW provided solutions which retained a significant percentage of solution viscosity after thermal aging and the average solution viscosity of the thermally aged solutions was about 6 times that of sea water at 250 F. This behavior indicates that the polymers are potentially useful in mobility control under hostile environment conditions.

Preliminary investigations of the analogous systems with calcium 2-acrylamido-2-methylpropanesulfonate [$Ca(AMPS)_2$] and aluminum 2-acrylamido-2-methylpropanesulfonate [$Al(AMPS)_3$] indicated that these salts were significantly less soluble in aqueous systems than the $Mg(AMPS)_2$ monomer. In view of this finding, the $Ca(AMPS)_2$ and $Al(AMPS)_3$ compositions were not extensively studied.

EXAMPLE XLVIII

This example describes the preparation of diamine salts of 2-acrylamido-2-methylpropanesulfonic acid (AMPS). The isolated salts or solutions of these salts can be prepared by neutralizing AMPS with selected diamines such as N,N,N',N'-tetramethylethylene diamine (TMEDA), N,N,N',N'-tetramethyl-1,4-butanediamine (TMEKBA) and N,N,N',N'-tetramethyl-1,6-hexanediamine (THDA).

Thermal aging test data are also presented in this example for polymers derived from the diamine/AMPS salts.

(a) Preparation of TMEDA(AMPS)₂

A solution of AMPS was prepared in a 500 mL Erlenmeyer flask by mixing 250 mL of N,N-dimethylformamide (DMF) with 50 g (0.24 mole) AMPS. A separate solution of N,N,N',N'-tetramethylethylenediamine (TMEDA) in DMF was prepared by mixing 14.6 g (0.12 mole) TMEDA with 50 mL of DMF in a 250 mL flask. The stirred DMF solution of AMPS was cooled in an ice bath during the dropwise addition of the TMEDA/DMF solution. After this addition was complete, the reaction mixture was stirred for another 15 minutes.

The total reaction mass was poured into 1000 mL of cyclohexane and the addition of 280 mL of methanol gave a two phase mixture. The top phase was separated, diluted with 1000 mL of acetone and allowed to stand 16 hours to complete the precipitation of the diamine/AMPS salt. The precipitate was removed by suction filtration and dried in vacuo at ambient temperature to give 43.8 g of TMEDA(AMPS)₂ (68% yield).

(b) Preparation of TMEBA(AMPS)₂

A solution of N,N,N',N'-tetramethylbutanediamine (TMEBA) was prepared in a 500 mL Erlenmeyer flask by mixing 300 mL of DMF with 22.2 g (0.15 mole) of TMEBA. This solution was stirred in an ice bath and to this cold solution was added portion-wise a total of 60 g (0.29 mole) of powdered AMPS (commercial grade). After all the AMPS had been added, a thick slurry was obtained.

This slurry was diluted with 150 mL of methylethyl ketone before pouring the entire reaction mass into a mixture of 500 mL of cyclohexane and 350 mL of methylethyl ketone. Precipitation of the TMEBA(AMPS)₂ salt was allowed to continue for one hour and forty-five minutes before suction filtration. The product was washed twice with 100 mL portions of cyclohexane and dried in vacuo at 35° C. to give 76.8 g TMEBA(AMPS)₂ (95% yield).

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(c) Preparation of THDA(AMPS)₂
This salt N,N,N',N'-tetramethylhexanediammonium 2-acrylamido-2-methylpropanesulfonate [THDA-(AMPS)₂] was prepared in essentially the same manner as the above TMEDA(AMPS)₂ and TMEBA(AMPS)₂ salts.

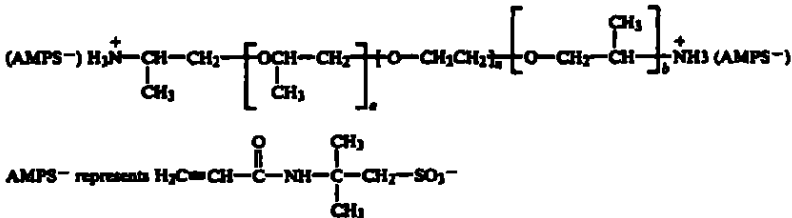
Polymers of the various diamine/AMPS salts were prepared in accordance with conventional solution polymerization technology using total solids levels of 20-30% in distilled water at ambient temperature with about 0.1 phm of initiator. As indicated hereinabove the cited weight percentages of monomer units in the polymer compositions reflects the relative weights of monomers charged to the polymerization zone.

The gelled reaction masses from the polymerizations were mixed with sufficient synthetic North Sea water to

was carried out at 35% total solids with 5 parts by weight of TMEBA/(AMPS)₂ and 95 parts by weight of NaAMPS prepared from refined grade AMPS. The aged solution viscosity value of 5.51 is about 19 times the viscosity of sea water at 250 F which indicates that this system possesses potential as a mobility control agent under hostile environment conditions.

EXAMPLE XLIX

This example describes the preparation of AMPS salts of diamines which are characterized by the presence of an oligomeric moiety between the amino groups. These compounds are poly(oxyethylene) diamines derived from propylene oxide-capped polyethylene glycol. The AMPS salts of these diamines have the structures shown below,



prepare 0.1 weight percent and 0.25 weight percent solutions for solution viscosity measurements. Test results are summarized in Table LXII.

The diamines used in neutralizing AMOS are available from Texaco Chemical Co. and are known as Jeffamine Ed Compounds. The diamines ED-600, ED-900 and

TABLE LXII

Run No.	Polymers of Diamine/(AMPS) ₂ Salts in Synthetic North Sea Water (SNSW)				IV (0.1) SNSW 25 C.	(0.25 SNSW) cP	
	TMEDA ^a (AMPS) ₂	Monomer Units (Wt %)		THDA ^d (AMPS) ₂		Unaged	Aged
		NaAMPS ^b	TMEBA ^c (AMPS) ₂				
1	5	95	0	0	9.55	3.13#	2.87#
2	10	90	0	0	8.81	2.93+	1.35+
3*	10	45	0	0	8.23	1.67	0.95
4	0	100	0	0	5.8	1.30	0.98
5	0	97	3	0	6.2	1.53	1.42
6**	0	95	5	0	6.0	1.36	1.25
7	0	90	10	0	5.9	1.40	1.31
8	0	85	15	0	4.3	1.50	1.43
9	0	100	0	0	6.3	1.44	1.41
10	0	95	0	5	6.2	1.39	1.34
11	0	90	0	10	6.0	1.36	1.30

^aThe composition was 10 wt % VP, 15 wt % Am, 10 wt % TMEDA (AMPS)₂ and 45 wt % NaAMPS.
^bA duplicate sample of this composition prepared from refined grade AMPS gave an unaged solution viscosity of 3.81 and an aged solution viscosity of 3.51.
^cUnaged value on a duplicate sample was 2.43 and aged value was 1.94.
^dUnaged value on duplicate sample was 2.40 and aged value was 1.94.
^eTMEDA(AMPS)₂ represents the salt of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and N,N,N',N'-tetramethyl-1,4-bisazobenzene.
^fNaAMPS represents sodium 2-acrylamido-2-methylpropanesulfonate.
^gTMEBA(AMPS)₂ represents the salt of AMPS and N,N,N',N'-tetramethyl-1,4-bisazobenzene.
^hTHDA(AMPS)₂ represents the salt of AMPS and N,N,N',N'-tetramethyl-1,6-bisazobenzene.

Referring to the results in Table LXII, it is evident that relatively small loadings of the diamine (AMPS)₂ monomer in copolymerizations with NaAMPS (from commercial grade AMPS) provided potentially useful modified polymers. After thermal aging, solutions of these modified polymers in SNSW exhibited good retention of solution viscosity (see aged and unaged viscosity values). The average aged viscosity of the diamine (AMPS)₂/NaAMPS copolymer solutions was about 5 times the viscosity of SNSW at 250 F. This behavior shows that the polymers are useful in mobility control under hostile environment conditions.

The best performer in Table LXII is found in run 6**. In the preparation of the 5/95 TMEBA/(AMPS)₂ salt, refined grade AMPS was used. The copolymerization

ED-2001 were used and their descriptors are shown below.

Diamine	n Range	(a + b) Range	Approx. Mol. Wt.
ED-600	8-9	2-3	600
ED-900	15-16	2-3	900
ED-2001	40-41	2-3	2000

Thermal aging test data are also presented in this example for polymers derived from the oligomeric diamine/AMPS salts.
(a) Preparation of ED-600/(AMPS)₂ monomer

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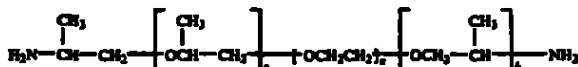
A charge of 63.3 g (0.202 equivalent, 4.7% excess) of ED-600 and 97.6 g of distilled water was placed in a 400 mL beaker. This stirred mixture was chilled in an ice bath during the gradual addition of 40 g (0.193 equivalent) of 2-acrylamido-2-methylpropanesulfonic acid (AMPS). The reaction mixture temperature was maintained at a temperature of less than 30° C as the AMPS

polymer solutions was about 3.5 times the viscosity of SNSW at 250 F. This behavior indicates that the subject polymers are useful in hostile environments, i.e., at temperatures in excess of 170 F and in the presence of greater than 500 ppm divalent metal cations. Most remarkable is the essentially 100 percent retention of viscosity on high temperature aging.

TABLE LXIII

Run No.	Polymers of Diamine/(AMPS) ₂ Salts in Synthetic North Sea Water (SNSW)				(0.25 SNSW) cP	
	Monomer Units (Wt %)				Unaged	Aged
	ED-600 ^a (AMPS) ₂	ED-900 ^b (AMPS) ₂	NaAMPS	ED-2001 ^c (AMPS) ₂		
12	2	0	98	0	6.3	1.29
13	5	0	95	0	5.8	1.16
14	10	0	90	0	5.2	0.95
15	0	2	98	0	5.6	1.17
16	0	10	90	0	5.0	0.9
17	0	0	98	2	5.5	1.11
18	0	0	90	10	4.9	1.0

^aED-600 (MW ca. 600) is an oligomeric diamine described by the formula



wherein n is in the range of 3-9 and $(m+p)$ is in the range of 2-1.

^bED-900 (MW ca. 900) is described by the above formula wherein n is 3-16 and $(m+p)$ is 2-3.

^cED-2001 (MW ca. 2000) is described by the above formula wherein n is 40-41 and $(m+p)$ is 2-3.

was added. After all the AMPS had been added, the reaction mixture was stirred for an additional 30 minutes. The measured pH of this mixture was 7.68. This procedure provided an aqueous mixture of ED-600/(AMPS)₂ containing approximately 50 weight percent of the ED-600/(AMPS)₂ monomer. Aliquots of this solution were used in the solution polymerizations.

(b) Preparation of ED-900/(AMPS)₂ monomer

This monomer was prepared in essentially the same manner as the ED-600/(AMPS)₂ monomer described above. A stock solution of ED-900/(AMPS)₂ in water (50 weight percent) was prepared. Aliquots of this solution were used in the solution polymerizations. The pH of this stock solution was 7.78.

(c) Preparation of ED-2001/(AMPS)₂ monomer

This monomer was prepared in essentially the same manner as the ED-600/(AMPS)₂ and ED-900/(AMPS)₂ monomers. A stock solution of ED-2001/(AMPS)₂ in water (50 weight percent) was prepared. Aliquots of this solution were used in the solution polymerizations. The pH of this stock solution was 8.56.

Polymers of the various oligomeric diamine AMPS salts were prepared in accordance with conventional solution polymerization technology using total solids levels of 20-35% in distilled water at ambient temperature with about 0.1 phm of initiator. As indicated above, the cited weight percentages of monomer units in the polymer compositions reflects the relative weights of monomers charged to the polymerization zone.

The gelled reaction masses from the polymerizations were mixed with sufficient synthetic North Sea water to prepare 0.1 weight percent and 0.25 weight percent solutions for solution viscosity measurements. Test results are summarized in Table LXIII.

Referring to the results in Table LXIII, it is evident that the oligomeric diamine/AMPS salts in relatively small amounts yielded copolymers with NaAMPS which are useful as hostile environment polymers. After thermal aging in synthetic North Sea water, solutions of these modified polymers exhibited good retention of solution viscosity (cf. aged and unaged viscosity values). The average aged viscosity values of the modified

EXAMPLE I

This example describes the organic crosslinking (gelation) of polymers useful in a hostile environment characterized by the presence of pendant —CONH₂ groups along the polymer chain. The preferred crosslinking system is a combination of phenol and formaldehyde. The following polymers were tested: (a) poly(N-vinyl-2-pyrrolidone-co-acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate) (35/25/40) (wt/wt/wt) (VP/Am/NaAMPS), (b) poly(N-vinyl-2-pyrrolidone-co-acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate) (30/15/55) (wt/wt/wt) (VP/Am/NaAMPS), (c) poly(acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate) (40/60) (wt/wt) (Am/NaAMPS) and (d) poly(N-vinyl-2-pyrrolidone-co-acrylamide) (60/40) (wt/wt) (VP/Am).

Synthetic North Sea water was used as the aqueous medium in all of the experimental work. Synthetic North Sea water was prepared by dissolving the following amounts of salt in sufficient distilled water to give 18 liters of solution (SNSW):

NaCl	439.0 g
Na ₂ SO ₄	77.2 g
NaHCO ₃	3.7 g
MgCl ₂ ·6H ₂ O	193.9 g
CaCl ₂ ·2H ₂ O	29.6 g

Stock solutions of polymers were prepared in SNSW. In general, sufficient gel log polymer was dissolved in SNSW to give a polymer concentration of 10,000 ppm. For example, an 18.5 g sample of gel log polymer containing 35 weight percent polymer can be dissolved in sufficient SNSW to give about 647 g of 10,000 ppm polymer solution. This proved to be a convenient concentration for use in these gelation experiments.

Stock solutions of phenol and formaldehyde were prepared by mixing formalin solution (37 weight percent formaldehyde, 13.9 weight percent CH₃OH and 49.1 weight percent H₂O) and phenol (88 weight percent phenol, 12 weight percent water). The weight ratio

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of formaldehyde to phenol is preferably about 1:1 which corresponds to about a 3:1 molar ratio of formaldehyde to phenol. In order to obtain, e.g., a 1:1 wt/wt ratio of phenol to formaldehyde, 29.6 g of phenol (88 wt % C_6H_5OH) is combined with 70.4 g of formalin (37 wt % $HCHO$).

$$29.6 \times 0.88 = 26.0 \text{ g } C_6H_5OH$$

$$70.4 \times 0.37 = 26.0 \text{ g } HCHO$$

The 100 g of solution exhibited a density of about 1.076 g/mL. This stock solution contains about 260,000 ppm C_6H_5OH and about 260,000 ppm $HCHO$.

The preparation and thermal aging of $HCHO/C_6H_5OH$ crosslinked HE polymer gels was carried out in ampoules with a capacity of about 62.5 mL. The cylindrical glass ampoules were 23 mm OD $\times$ 225 mm in length, one end was sealed and to the other end was sealed a 6 mm OD $\times$ 80 mm long glass tube. This tube was sealed by a torch prior to incubation of the test samples. The total test sample in each run amounted to about 20 mL.

After the introduction of the polymer solution and the $HCHO/C_6H_5OH$ gelling agent, the ampoule was alternately purged with nitrogen and evacuated by a vacuum means 3 times at ambient temperature. The system was then chilled for 2 minutes in a salt water-ice bath and the purge/evacuation cycle was repeated.

The ice-salt water bath was replaced with an 85 F water bath and the system was allowed to warm up for about 2 minutes. The ampoule was gently shaken which resulted in the controlled bubbling of the polymer test sample. The ampoule was removed from the warm water bath and the system was adjusted to 1 atmosphere N_2 pressure.

The ampoule was re-cooled in the salt water-ice bath before repeating the N_2 purge/evacuation cycle. Before sealing off the ampoule with a torch, the pressure in the ampoule was adjusted to about 0.8 atmosphere N_2 .

The sealed ampoules containing about 20 mL of the polymer solution and the $HCHO/C_6H_5OH$ gelling system were incubated in an air-circulating temperature controlled oven. The ampoules were placed in an aluminum container equipped with a clamp-fastened top and the container was placed in the oven. Ampoules were removed from the oven at specified time intervals and the test fluids were observed in regard to their tendency to flow. Samples were incubated at 200 F, 250 F and 300 F.

If the gel fluid flowed the entire 225 mm length of the ampoule with the ampoule in a horizontal orientation, the fluid was considered not gelled (NG). As gelation progressed the gels were qualitatively evaluated by noting the tendency of the gels to flow as reflected by "tongue lengths." Zero on the tongue length scale being defined by the fluid level in the ampoule when the ampoule is in an upright position. Once the gelation had progressed to the point at which tongue lengths were on the order of $\frac{1}{2}$ " in the horizontal position, the gel was designated as hard (H—). If the tongue lengths were on the order of 1" in a tilted position 45° from the horizontal, the gel was designated as hard (H). If no gel movement was detectable with the ampoule in an inverted orientation, the gel was designated as very hard (VH).

Sample mixtures of polymers and the $HCHO/C_6H_5OH$ organic crosslinking (gelation) agent were pre-

pared, e.g., by mixing appropriate amounts of SNSW polymer solution and a gelling agent solution containing equal concentrations of formaldehyde and phenol. The total sample mixture in each run was on the order of 20 mL.

In the systems studied, the relative concentrations of formaldehyde and phenol (ppm) were about the same. The concentration of polymer in the test samples was about 10,000 ppm. In runs 1-6 and 10-12 (Table LXIV) the formaldehyde and phenol concentrations were in the range of 450 to 600 ppm. In runs 7-9 the phenol and formaldehyde concentrations were in the range of 2750 ppm.

Referring to the 200 F results in Table LXIV, i.e., runs 1, 4, 7 and 10, it is evident that all the polymers crosslinked to hard to very hard gels which exhibited good stability over a long period of time at 200 F. None of these gels had lost stability when the tests were terminated, respectively, at 35, 35, 155 and 99 days.

Referring to the 250 F results in Table LXIV, i.e., runs 2, 5, 8 and 11, it is evident that all the polymers except for Am/NaAMPS (40/60) (see run 8) crosslinked to hard or very hard gels which exhibited good stability over a long period of time at 250 F. None of the stable gels in runs 2, 5, and 11 had degraded when the tests were terminated, respectively, at 40, 40 and 99 days. The system in run 8 gave a relatively fast gelation rate but the gel exhibited significant syneresis and the test was terminated in about 19 days.

Referring to the 300 F results in Table LXIV, i.e., runs 3, 6, 9 and 12, it is evident that all the polymers except for Am/NaAMPS (40/60) (see run 9) crosslinked to hard or very hard gels which exhibited good stability over a long period of time at 300 F. None of the hard gels in runs 3, 6 and 13 had exhibited any syneresis when the tests were terminated, respectively, at 40, 40 and 99 days. The system in run 9 gave a fast gelation rate but the gel exhibited severe syneresis and the test was terminated in less than 3 days.

Attention is called to the relatively high concentrations of formaldehyde (2542 ppm) and phenol (2942 ppm) used with the Am/NaAMPS (40/60) copolymer in runs 7, 8 and 9. In runs 1-6 and 10-12 the formaldehyde and phenol concentrations varied over the range of about 450 ppm to about 600 ppm. Perhaps the higher concentrations of the $HCHO$ and phenol at the higher temperatures of 250 F and 300 F resulted in an undesirable overtreatment reflected in the syneresis of the gel. The syneresis sometimes results if the gel is too highly crosslinked. At 200 F, however, the higher concentrations of $HCHO$ and phenol (see run 7) resulted in a very hard gel which had exhibited no syneresis after 155 days at 200 F.

In preliminary studies the polymer in Table XVII were crosslinked with $HCHO/C_6H_5OH$ in fresh water at 200 F, 250 F and 300 F. The very hard gels exhibited no syneresis in aging studies at 200 F, 250 F and 300 F.

The results in Table LXIV, especially in runs 1-6 and 10-12 indicate that the gels produced by the $HCHO/C_6H_5OH$ crosslinking of stable polymers bearing pendant $-CONH_2$ groups in SNSW are useful for permeability contrast corrections under harsh environment conditions, i.e., temperatures in excess of 170 F and hardness cation concentrations in excess of 500 ppm.

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TABLE LXIV

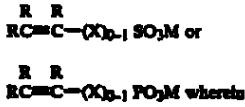
RE Polymer	Organic Crosslinked Polymers in Synthetic North Sea Water					
	Run No.	Oven Temp. °F	Detectable Gel (Days) ^a	Gelation Appeared Completed ^c	Character of Gel/	Length of Test (Days)
VT ^a /Am ^b /NaAMPS ^c (35/25/40)	1 ^d	200	4	9.0	Hard	33
	2	250	1.5	3.5	Very Hard	40
	3	300	0.75	2.8	Very Hard	40
VP/Am/NaAMPS (30/15/55)	4 ^e	200	6.0	11.0	Hard	35
	5	250	1.8	4.0	Hard	40
	6	300	0.85	3.0	Hard	40
Am/NaAMPS (40/60)	7 ^f	200	3.0	20	Very Hard	155
	8	250	<1.0	<3.0	Synersesed ^g	<19
	9	300	<0.6	0.6	Synersesed ^g	<2.7
VP/Am (60/40)	10 ^h	200	20	64	Hard	99
	11	250	3	14	Very Hard	99
	12	300	1	3	Hard	99

^aVP represents N-vinyl-2-pyrrolidone.
^bAm represents acrylamide.
^cNaAMPS represents sodium 2-acrylamido-2-methylpropane-sulfonate.
^dThese times indicate the approximate number of days of incubation required before the gel fluid did not flow the 225 mm length of the cylindrical ampoule in the horizontal orientation.
^eThese times indicate the approximate number of days of incubation required to reach the maximum firmness of the gel.
^fThe H or hard gels provided tensile lengths on the order of 1" with the ampoule in a tilted orientation of 45° from the horizontal. The VH or very hard gels showed no gel movement with the ampoule in a 90° inverted orientation.
^gThe gels undergoing synerses exhibited a layer of fluid which had separated from the body of the gel. The more severe the synerses, the greater the relative volume of the separated fluid phase. Aging tests were terminated as soon as synerses was detectable.
^hConcentrations of polymer, formaldehyde and phenol, respectively were 9977 ppm, 362 ppm and 588 ppm.
ⁱConcentrations of polymer, formaldehyde and phenol, respectively were 9978 ppm, 577 ppm and 583 ppm.
^jConcentrations of polymer, formaldehyde and phenol, respectively were 9996 ppm, 2542 ppm and 2642 ppm.
^kConcentrations of polymer, formaldehyde and phenol, respectively were 9976 ppm, 434 ppm and 451 ppm.

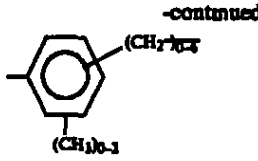
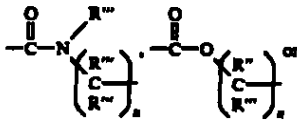
While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby, but is intended to cover all the changes and modifications within the spirit and scope thereof

That which is claimed is

1 A process comprising injecting a surfactant system into a subterranean formation under hostile conditions defined as having a formation temperature and multivalent cation concentration above the infinite days line of FIG 14 through an injection well to form a micellar composition or microemulsion in said formation, thereafter injecting a mobility buffer slug comprising a water-soluble polymer produced from a monomer composition comprising at least one monomer selected from the group consisting of hydrophilic N-vinyl amides and hydrophilic components of the formula



R is methyl, ethyl or H, provided further that at least one of the R groups on the terminal carbon of the vinyl group is H and the other is H or methyl, M is selected from the group consisting of H, Na⁺, K⁺, Li⁺, R⁺, N⁺, Ca⁺⁺, Mg⁺⁺, Zn⁺⁺, Sr⁺⁺, Fe⁺⁺, Mn⁺⁺, and +NH₃R¹NH₃⁺ where R¹ is a 1-20 carbon atom divalent hydrocarbon radical, R⁺ is H, -ROH or a 1-3 carbon atom alkyl group; wherein X is selected from



where n is an integer of 1-5, and R⁺ is a 1-3 carbon atom alkyl group, or H, thereafter introducing a drive fluid, and recovering oil from a spaced apart production well

2. A process according to claim 1, wherein said conditions are further defined by a concentration of said divalent ions within the range of 1000 to 100,000 ppm.

3. A process comprising injecting a surfactant system into a subterranean formation under hostile conditions defined as having a formation temperature and multivalent cation concentration above the infinite days line of FIG 14 through an injection well to form a micellar composition or microemulsion in said formation, thereafter injecting a mobility buffer slug comprising a polymer produced from a monomer composition comprising at least one monomer selected from the group consisting of hydrophilic N-vinyl lactams, hydrophilic vinyl-containing sulfonate salts and the corresponding acids thereof, thereafter introducing a drive fluid, and recovering oil from a spaced apart production well.

4. A process according to claim 3 wherein said surfactant composition comprises a petroleum sulfonate surfactant and an alcohol cosurfactant.

5 A process according to claim 4 wherein said polymer is a homopolymer of N-vinyl-2-pyrrolidone.

6. A process according to claim 4 wherein said polymer is a copolymer of N-vinyl-2-pyrrolidone and an unsaturated amide.

7 A process according to claim 6 wherein said unsaturated amide is selected from the group consisting of acrylamide and N,N-dimethylacrylamide.

8. A process according to claim 6 wherein said monomer composition comprises N-vinyl-2-pyrrolidone and sodium 2-acrylamido-2-methylpropane-sulfonate

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9 A process according to claim 3 wherein said monomer composition comprises N-vinyl-2-pyrrolidone.

10 A process according to claim 3 wherein said monomer composition comprises said N-vinyl lactam, said vinyl-containing sulfonate salt and an unsaturated amide

11 A process according to claim 3 wherein said monomer composition comprises sodium 2-acrylamido-2-methylpropanesulfonate

12 A process according to claim 11 wherein said monomer consists essentially of said sodium-2-acrylamido-2-methylpropanesulfonate

13 A process according to claim 11 wherein said monomer composition comprises sodium 2-acrylamido-2-methylpropanesulfonate and an unsaturated amide selected from acrylamide and N,N-dimethylacrylamide

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[54] OIL RECOVERY PROCESS UTILIZING GRAVITATIONAL FORCES

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[51] Int. Cl.⁴ .. E21B 43/22

[52] U.S. Cl. .. 166/273; 166/269

[58] Field of Search .. 166/268, 269, 273

[56] References Cited

U S. PATENT DOCUMENTS

3,139,929	7/1964	Habermann	-	166/273
3,221,810	12/1965	Marz	-	166/269
3,302,710	2/1967	Odeh	-	166/269
3,667,545	6/1972	Knight	-	166/273 X
3,700,031	10/1972	Germer, Jr et al	-	166/273 X
3,710,861	1/1973	Steeg	-	166/273 X
3,977,470	8/1976	Chang	-	166/273
4,079,785	3/1978	Hessert et al	-	166/273
4,122,895	10/1978	Sitton et al	-	166/273 X
4,240,504	12/1980	Reed	-	166/273
4,230,961	2/1981	Morse et al	-	166/273 X

FOREIGN PATENT DOCUMENTS

51706	5/1969	Romania	-	166/273 X
1021607	3/1966	United Kingdom	-	166/268

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Michael G. Gilman, Stanislaus Aksman

[57] ABSTRACT

There is disclosed a method of recovering oil from a subterranean oil formation having the vertical thickness of 40 ft or more. The method exploits the effect of gravity on the various slugs of diverse materials injected into the oil column of the formation. The method comprises injecting a surfactant slug into the lower 50-75% of the vertical thickness of the oil column, then injecting a slug of a mobility control polymer into the upper 50-75% portion of the thickness of the oil column, followed by the injection of a slug of a drive fluid over substantially the entire vertical thickness of the oil formation. Optionally, a low-salinity pre-flush slug may be injected to remove high salinity water from contact with the oil and an alkaline pre-treat solution may be injected to remove divalent ions prior to the injection of the surfactant slug.

31 Claims, No Drawings

OIL RECOVERY PROCESS UTILIZING GRAVITATIONAL FORCES

BACKGROUND OF THE INVENTION

I Field of the Invention

The invention is directed to an improved method of recovering oil from underground, relatively thick oil formations. More particularly, the invention is directed to the recovery of oil from such formations wherein a surfactant and a mobility control agent, alone or with additional optional agents, are injected into the formation at predetermined, vertically-spaced portions of the oil formation.

II Description of the Prior Art

In the recovery of oil from subterranean formations, the oil is usually initially extracted by primary recovery techniques which rely on the naturally-occurring reservoir pressure forces to provide the pressure necessary to recover the oil. Once the primary recovery techniques are completed, a substantial amount of oil may be present in the reservoir, depending on the reservoir conditions. To recover this oil, secondary recovery techniques have been employed in the past. One of such secondary recovery techniques involves waterflooding, whereby water is injected into the porous rock, thereby displacing the brine and part of the oil in the portions of the formation contacted by the waterflood. As injected water invades the porous rock, an oil-water transition zone is created wherein the increasing saturation by the water causes the rupture of the continuous oil filaments. If the rock-oil-water system is preferentially water wet, the oil that remains is in the form of discontinuous globules or ganglia surrounded by rock and isolated by water. This oil is trapped by capillary forces and is normally referred to in the art as "residual oil". The residual oil communicates directly with water-saturated flow channels. It is known in the art that pores containing the residual oil contain very little water. The formation of the residual oil globules during the waterflooding process is dependent upon a number of criteria, such as oil-water interfacial tension and pore geometry. Tertiary oil recovery techniques have been developed in the past to recover this residual oil. In the tertiary oil recovery it is essential that the water in the water-saturated flow channels be replaced with a different fluid which interacts with the oil in the trapped ganglia and causes at least a part thereof to be displaced and coalesce with other similarly-displaced globules of oil to form a continuous oil stream which is forced to flow in the formation and then is recovered at the surface thereof, e.g., through a suitable well.

Various surfactants have been used in the past in the tertiary oil recovery techniques to cause the residual oil globules to be displaced and subsequently coalesce with other similarly-displaced oil globules to form a continuous oil flow, as described, e.g., by Reed et al, in "Some Physicochemical Aspects of Microemulsion Flooding: A Review", pages 383-437 of "Improved Recovery By Surfactant and Polymer Flooding", AMERICAN INSTITUTE OF CHEMICAL ENGINEERS SYMPOSIUM ON IMPROVED OIL RECOVERY BY SURFACTANT AND POLYMER FLOODING, Kansas City, Kans., 1976, Published by Academic Press, Inc., New York, 1977, the entire contents of which are incorporated herein by reference.

Petroleum sulfonates, usually obtained by subjecting hydrocarbons, such as crude oil or partially refined oil,

to sulfonation conditions are known in the art as effective surface active agents used in enhanced oil recovery (EOR) applications. Various sulfonates and the use thereof as surface acting agents in the enhanced oil recovery applications are disclosed by Ahearn et al, U.S. Pat. No. 3,302,713, Patton, U.S. Pat. No. 3,373,808, Jones, U.S. Pat. No. 3,506,071, Gale, U.S. Pat. 3,861,466, and Aude et al, U.S. Pat. No. 4,290,973. Additionally, other materials known in the art can also be used as surfactants to free the oil and coalesce the dispersed globules thereof into a continuous stream. Such suitable other surfactants include, but are not limited to synthetic alkylaryl sulfonates, as described in U.S. Pat. No. 3,994,342, internal olefin and alpha-olefin sulfonates described in U.S. Pat. No. 4,549,607, propoxylated ethoxylated alcohol or alkylphenol ether sulfates and sulfonates described in U.S. Pat. No. 3,977,471, aliphatic and aromatic carboxylates described in U.S. Pat. No. 4,556,495, and nonionic surfactants, as described by Gracusa et al in the paper "Criteria for Structuring Surfactants to Maximize Solubilization of Oil and Water: Part I-Commercial Nonionics", which appeared in *Soc. of Petr. Eng. Journal* (Oct, 1982), 22, 743-749.

The entire contents of all of the above patents and publications are incorporated by reference herein.

The surfactants used in the large volumes necessary to recover a substantial proportion of the residual oil substantially increase the overall cost of oil recovery. Accordingly, it is important to minimize, when possible, the amount of the surfactant used to recover the residual oil from a particular formation. Similarly, mobility control polymers, also used in the past to control the flow of drive fluid and/or flooding fluids into the oil formation also add substantially to the overall cost of the oil recovery operation. Accordingly, it is also important to minimize the amount of such mobility control polymers used in the tertiary recovery operations.

Thus, a need still exists in the art for providing an improved process of recovering oil from underground formations wherein the amount of the surfactants and mobility control polymers used in the oil recovery process is substantially reduced.

SUMMARY OF THE INVENTION

A method of recovering oil from a subterranean oil formation having the vertical thickness of at least 40 feet utilizes at least one injection well and at least one production well spaced apart from the injection well. The method comprises the consecutive steps of:

- (1) injecting a surfactant slug into the lower 50-75% vertical thickness of the oil column,
- (2) injecting a slug of a mobility control polymer into the upper 50-75% portion of the vertical thickness of the oil column,
- (3) injecting a drive fluid throughout substantially 100% of the vertical thickness of the oil column, and,
- (4) recovering oil from the production well.

DETAILED DESCRIPTION OF THE INVENTION

The injection of the surfactant and the mobility control polymer slugs into the oil column at the vertical thickness regions specified herein promotes the maximum utilization efficiency of the surfactant and the mobility control polymer since the gravity forces acting on the respective slugs of these materials tend to maximize the recovery of the oil upon injection of a limited

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amount of chemicals into the underground formation. The surfactant desirably forms a middle phase microemulsion with the reservoir brine and oil. The density of the microemulsion is greater than that of the oil in the formation but lower than that of the water; accordingly, the microemulsion and oil released by the microemulsion tend to travel upwards in the vertical oil formation.

The polymer slug is injected after the surfactant slug into the upper 50 to 75% portion of the vertical thickness of the oil column because, at the time of the injection of the polymer slug, most of the oil in the formation is either located in the upper portion of the oil column or is migrating in that direction. Accordingly, the injection of the polymer slug into the upper region of the oil column maximizes the efficiency of the polymer. The injection of optional, additional slugs of diverse materials, discussed below, into the oil column at the relative vertical elevations, specified below, of the oil column is also designed to obtain maximum advantage from the gravitational forces acting on such slugs, thereby maximizing the efficiency of the injection thereof. The term "vertical thickness of the oil column", as used herein, designates the thickness of the portion of the formation containing the oil, measured in a vertical direction from the top to the bottom of that portion of the formation. To fully utilize the beneficial effect of the gravitational forces on the oil recovery in the method of this invention, the subterranean oil column must have the vertical thickness of at least about 40 feet, preferably at least about 100 feet. The oil formation comprising the oil column must additionally have the following characteristics: significant vertical permeability, desirably at least one-tenth or more of the horizontal permeability, and should not contain extensive shale laminations or other barriers to vertical fluid migration.

The surfactants used in the present invention are any of the well known surfactants used heretofore in enhanced oil recovery applications. Thus, sulfonates produced by sulfonating hydrocarbons can be used as the surfactants. Suitable sulfonates are those of Aude et al, U.S. Pat. No. 4,290,973, Ahearn et al, U.S. Pat. No. 3,302,713, Gale, U.S. Pat. No. 3,861,466 and Ahearn et al, U.S. Pat. No. 3,283,812, the entire contents of all of which are incorporated herein by reference. Suitable sulfonates used in the invention are those having a solubilization ratio of about three or higher. The solubilization ratio is defined as V_o/V_n , wherein V_o is the volume of oil solubilized by a unit of volume of petroleum sulfonate reactant, V_n in a middle phase microemulsion at "midpoint" or "optimal salinity". The solubilization ratio and the method of calculating thereof are described by Reed et al in the aforementioned paper entitled "Some Physicochemical Aspects of Microemulsion Flooding: A Review".

Other materials may also be used as surfactants. For example, synthetic alkylarylsulfonates, such as alkylbenzene-, alkyltoluene- or alkylxylene-sulfonates, e.g. Enordet LXS (linear alkyl ortho-xylene sulfonates) offered by Shell Chemical Company; internal olefin or alpha olefin sulfonates, as e.g. Enordet IOS or AOS series surfactants offered by Shell Chemical Company; ethoxylated alcohol ether sulfates or sulfonates, such as Shell Chemical Neodol 25-3S and Ethyl Corporation EOR 100, respectively; ethoxylated alkyl-phenol ether sulfates or sulfonates, such as Alipal CO 436 offered by GAF Corporation and Dodiflood V3620 offered by Hoechst chemical Co., respectively; propoxylated ethoxylated alcohol and alkylphenol ether sulfates and

sulfonates, such as those described in US Pat No 3,977,471, which are not yet offered as commercial surfactants, and ethoxylated alcohol and alkylphenol carboxylates, such as synperonic A3C and synperonic NP3C surfactants, respectively, offered by Imperial Chemical Industries. These and other surfactants proposed for use in enhanced oil recovery processes may be employed in gravity-assisted chemical flood process described herein.

The surfactant is normally used as a water additive in an aqueous solution, but may be injected as a water external microemulsion, or as an oil external microemulsion. Suitable concentrations of surfactants in the surfactant slug range from about 0.01% by weight to about 12% by weight, preferably about 0.1 to about 2.0% by weight. The upper limit of this range is usually determined by the solubility of the surfactant in a field brine, and by the fact that the use of larger concentrations may significantly increase the overall cost of the oil recovery operation. The aqueous solution of the surfactant may be formed prior to the injection of the solution into the formation or it may be formed in situ by injecting a separate stream of the surfactant into the aqueous water slug or slugs injected separately into the formation. The addition of the surfactant to the aqueous water slug may be continuous or discontinuous without departing from the scope of the invention, so long as the average concentrations of the surfactant in the surfactant slugs injected into the formation are maintained in the aforementioned range.

The surface-active character and oil displacement efficiency of the aqueous surfactant solution are substantially enhanced by incorporating into it small amounts of water-soluble salts, such as sodium, potassium or ammonium salts. As little as 0.1 weight % of sodium chloride, for example, may markedly improve the surface activity of petroleum or synthetic alkylaryl sulfonate mixtures. Preferred concentrations of sodium chloride for these surfactants which may optionally be used herein are between about 0.3 weight % to about 5 weight %, preferably about 0.4 weight % to about 2 weight %. Salt concentrations in excess of about 5 weight % become detrimental, since they tend to "salt out" these surfactants from the aqueous medium, thereby considerably reducing the effective concentration of surfactants at the flood front and rendering them less efficient. Desired salinity for surfactants, other than the synthetic or alkylaryl surfactants, which may be employed in this process may range up to about 15 to about 20%, depending upon the optimal salinity of the surfactant species. The injection of the surfactant slug is continued normally until 5 to 50 percent of the reservoir pore volume (PV) has been injected. The volume of surfactant injected will depend upon the surfactant concentration. The total surfactant injected, stated in terms of the product of the surfactant concentration (%) and slug size (% PV), is normally in the range of about 10 to about 100, preferably about 10 to about 50. The presence of polyvalent ions, such as calcium, in the water-surfactant mixtures of the invention is undesirable (if a petroleum or synthetic alkylaryl sulfonate surfactant is employed) and generally should be minimized. When this is not feasible, the aqueous solution of the surfactant should be treated appropriately so as to reduce the concentration of the polyvalent ions.

The mobility control polymer injected in the second step of the method of the present invention may be any one or a combination of the polymers well known in the

art for controlling the mobility of the drive fluid slug, and it is injected into the formation after the injection of the surfactant slug is completed. The mobility control polymer slug prevents, or at least minimizes, fingering of drive fluid into the surfactant slug and the channeling of fluids into the more permeable regions of the formation, thereby directing most of the drive fluid into contact with the oil and recovering a substantial proportion of the oil. Suitable polymers used as the mobility control agents include, but are not limited to, xanthan gum or natural polysaccharide polymers, such as Xanflo polymer offered by Kelco, or polyacrylamide synthetic polymers, such as Dow Pusher polymers offered by Dow Chemical Company. Preferred polymers are partially hydrolyzed polyacrylamide or xanthan polysaccharide polymers. The concentration of the polymer in the second step of the invention is normally about 100 to about 3000 ppm, preferably about 300 to about 1000 ppm. The concentration will normally be sufficient to provide a polymer solution mobility (k/μ) less than the minimum mobility of the oil/water bank being displaced. In this respect, k is the effective permeability of the oil column to the polymer solution of viscosity μ . The injection of the mobility control polymer slug is continued until about 10% to about 100%, preferably about 10% to about 50% of the reservoir pore volume is injected.

The salinity of the mobility control polymer slug should be lower than the critical salinity for establishing a type III phase environment by the surfactant/brine/oil system of the reservoir. For a petroleum sulfonate or alkylaryl sulfonate surfactant, the salinity of the polymer drive solution is normally within the range of about 0.05 to about 2.0%, preferably within the range of about 0.2 to about 1.0%.

After the injection of the mobility control polymer slug is completed, a slug of drive fluid is injected substantially into the entire vertical thickness of the oil column. The drive fluid is any well known drive fluid used in the enhanced oil recovery applications. Thus, the drive fluid may be a gas or water which displaces the oil, previously freed by the surfactant injection, towards the production well. Normally, the drive fluid is water, or brine which may contain additives, such as alcohol or sacrificial agents employed to minimize retention of surfactant and polymers. The injection of the drive fluid is continued to effect the displacement of formation oil through the production well until either all of the oil has been displaced from the formation or until the economical limit of the ratio of the drive fluid to formation oil has been reached. In a preferred embodiment, using petroleum or synthetic sulfonate surfactants, the drive fluid is low salinity water, having the salinity, i.e., the salt concentration, of about 0.05% to about 2.0%, preferably about 0.2 to about 1.0%.

If the method of the present invention employs a petroleum or alkylaryl sulfonate to recover oil from an oil formation containing high salinity brine (3% or more), it is necessary to inject a low salinity pre-flush slug, prior to the injection of the surfactant, substantially into the entire vertical thickness of the oil column and, if the oil column is positioned on top of an underlying high salinity aquifer in communication with the oil column, into some portion of the aquifer immediately underlying the line of the oil-water contact. The function of the low salinity pre-flush slug is to displace the high salinity water in the formation away from the vicinity of injection wells, so that the subsequently-

injected surfactant in the surfactant slug is not precipitated by the high salinity water. The composition of the low salinity pre-flush slug is such that it establishes an optimal salinity level within the oil column for the operation of the surfactant injected thereafter. The pre-flush slug comprises a low salinity water, typically fresh water to which sodium chloride has been added, or a softened field brackish water. The salinity of the pre-flush slug is generally about 0.1 to about 3.0% by weight, but for petroleum or alkylaryl sulfonates it is preferably about 0.4 to about 2.0% by weight. The amount of the low-salinity pre-flush slug injected is about 0.1 to about 1.0 pore volumes of the oil reservoir, depending upon reservoir characteristics, preferably it is about 0.2 to about 0.5 of the oil reservoir pore volume. The fractional height of the aquifer included in the pre-flush injection depends upon such reservoir factors as specific permeability of the rock, the ratio of the vertical to horizontal permeability, defined as permeability measured in the vertical direction to permeability measured horizontally to the reservoir layering (strata), reservoir thickness, well spacing, salinity of the aquifer, fraction of the oil-bearing reservoir volume to be surfactant-flooded and other factors peculiar to each oil reservoir, as will be apparent to those skilled in the art, and which will dictate the depth in the aquifer to which the pre-flush slug must be injected. However, the vertical portion of the aquifer, adjoining the oil column, to be pre-flushed is usually at least 10% and not more than 50% of the height of the oil column. The low-salinity, pre-flush slug is designated herein as step (A) and, if employed, it is injected in the method of the present invention immediately ahead of step 1, or step A1, alkaline pre-treat solution injection, if the latter is employed.

Optionally, the concentration of the divalent ions remaining within the reservoir after the pre-flush slug may be reduced by injecting a slug of an alkaline pre-treat solution into the formation. Such an alkaline pre-treat solution may contain any well known agents, used in the past to remove or neutralize divalent ions, dissolved in an aqueous base. Suitable agents are sodium carbonate or sodium orthosilicate, and the concentration of such agents in the pre-treat solution is generally in the range of 0.1 to 1.0%, desirably in the range of 0.2 to 0.5%. The alkaline agents may be supplemented by added NaCl to adjust total salinity of the pretreat slug to near optimal salinity of the surfactant utilized in the process. The alkaline pre-treat solution may be injected into the formation normally until 5 to 50% of a pore volume (desirably 10 to 20% PV) has been injected. The alkaline pre-treat solution injection step is referred to herein as step (A1) and it is conducted immediately before step (1) of the method of the present invention. The alkaline pretreat solution is injected into the entire vertical thickness of the oil formation.

If the process of the invention is used to recover oil from an oil formation positioned on top of the aquifer, the alkaline pre-treat solution is not injected into the aquifer.

The salinities of the low salinity pre-flush solution, surfactant slug, and polymer drive are generally selected to maintain the surfactant in a Type III phase environment over as long a distance as practical. The middle and upper phase microemulsions produced within the Type III phase environment are less dense than brine and more dense than oil. Accordingly, they will tend to migrate upward towards the existing oil-water boundary in the reservoir, releasing oil previ-

ously trapped by capillary forces in the lower portion of the oil column as it is contacted. The released oil will also tend to migrate upwardly to the top of the reservoir. In this connection, the term "Type III Phase Environment" is used herein to designate the salinity interval in which a three phase system consisting of brine, a middle phase microemulsion, and oil may be formed by mixing the surfactant, the oil, and the brine with the reservoir.

For the purposes of exemplification, set forth below are the concentration and salinity limits, in % by weight, for the various slugs used in the process of the invention utilizing petroleum or alkylaryl sulfonate surfactants.

	General Range	Preferred Range
Preflush Salinity (1)	0.1-5.0%	0.4-2.0%
Pretreat Salinity (incl. alk. agt.) (1)	0.3-5.0%	0.4-2.0%
Pretreat Alk. Conc.	0.1-1.0%	0.2-0.5%
Surfactant Conc.	0.01-12%	0.1-2.0%
Surfactant Salinity (2)	0.3-5.0%	0.4-2.0%
Polymer Conc.	100-3000 ppm ACT	300-1000 ppm ACT
Polymer Salinity (3)	0.05-2.0%	0.2-1.0%
Drive Salinity (4)	0.05-2.0%	0.2-1.0%

(1) Preferred pre-flush and pretreat salinity is marginally higher than the optimal salinity for the surfactant employed. Pretreat salinity includes concentration of alkaline sacrificial agent, if any, and added NaCl.

(2) Preferred surfactant salinity is near optimal salinity for the surfactant employed or within the range of the critical lower salinity for Type III phase environment (lower limit) to the optimal salinity (upper limit).

(3) Preferred salinity for polymer drive is marginally lower than the critical lower salinity for Type III phase environment.

(4) The salinity may grade downward to a limiting lower salinity needed to prevent damage to injection wells from swelling clays.

In a preferred embodiment, the method of the present invention is conducted in an oil formation perforated by at least one injection well and at least one production well spaced apart from the injection well, with the two wells being in communication with each other.

It will be apparent to those skilled in the art that the specific embodiments discussed above can be successfully repeated with ingredients equivalent to those generically or specifically set forth above and under variable process conditions.

From the foregoing specification, one skilled in the art can readily ascertain the essential features of this invention and without departing from the spirit and scope thereof can adapt it to various diverse applications.

We claim

1. A method of recovering oil from a subterranean oil formation having the vertical thickness of at least about 40 feet, comprising an oil column which is a portion of the formation containing the oil, the formation containing at least one injection well and at least one production well spaced apart from said injection well, comprising the consecutive steps of

- (1) injecting a surfactant slug into the lower 50 to 75% vertical thickness of the oil column,
- (2) injecting a slug of a mobility control polymer into the upper 50 to 75% portion of the vertical thickness of the oil column,
- (3) injecting a slug of a drive fluid over substantially the entire vertical thickness of the oil column, and,
- (4) recovering oil from the production well.

2. A method of claim 1 wherein, prior to said step (1), there is conducted the following step

(A) injecting a pre-flush slug of a relatively low salinity water into the entire vertical thickness of the oil column.

3. A method of claim 2 wherein the pre-flush slug comprises a sodium chloride solution or softened field water and has the salinity of about 0.1 to about 5.0%.

4. A method of claim 3 wherein the surfactant slug comprises an aqueous solution of petroleum or alkylaryl sulfonate surfactants.

5. A method of claim 4 wherein the mobility control polymer comprises an aqueous solution of partially hydrolyzed polyacrylamide or xanthan polysaccharide polymers.

6. A method of claim 5 wherein, subsequently to said step (A), but prior to said step (1), there is conducted the following step

(A1) injecting an alkaline pre-treat solution slug substantially into the entire vertical thickness of the oil column.

7. A method of claim 6 wherein the alkaline pre-treat solution slug comprises an aqueous solution of the sodium carbonate or sodium orthosilicate.

8. A method of claim 5 wherein the drive fluid is a field brine, fresh water or a mixture thereof of salinity lower than necessary to produce a Type III phase environment for the surfactant/brine/oil system of the reservoir.

9. A method of claim 7 wherein the drive fluid is a field brine, fresh water or a mixture thereof of salinity lower than necessary to produce a Type III phase environment for the surfactant/brine/oil system of the reservoir.

10. A method of claim 8 wherein the salinity of the pre-flush slug is about 0.4 to about 2.0%.

11. A method of claim 10 wherein the salinity of the surfactant slug is about 0.4 to about 2.0%.

12. A method of claim 11 wherein the salinity of the slug of the mobility control polymer is about 0.2 to about 1.0%.

13. A method of claim 9 wherein the salinity of the pre-flush slug is about 0.4 to about 2.0%.

14. A method of claim 13 wherein the salinity of the surfactant slug is about 0.4 to about 2.0%.

15. A method of claim 14 wherein the salinity of the slug of the mobility control polymer is about 0.2 to about 1.0%.

16. A method of claim 2 wherein the oil column is in contact with an underlying body of water, and wherein the pre-flush slug is injected into at least a portion of the underlying body of water.

17. A method of claim 16 wherein the pre-flush slug is injected into a vertical thickness portion of the underlying body of water which is at least 10% of the vertical thickness of the oil column.

18. A method of claim 17 wherein the pre-flush slug is injected into a vertical thickness portion of the underlying body of water which is 50% or less of the vertical thickness of the oil column.

19. A method of claim 18 wherein the pre-flush slug comprises a sodium chloride solution or softened field water and has the salinity of about 0.1 to about 5.0%.

20. A method of claim 19 wherein the surfactant slug comprises an aqueous solution of petroleum or alkylaryl sulfonate surfactants.

21. A method of claim 20 wherein the mobility control polymer comprises an aqueous solution of partially hydrolyzed polyacrylamide or xanthan polysaccharide polymers.

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22. A method of claim 21 wherein, subsequently to said step (A), but prior to said step (1), there is conducted the following step

(A1) injecting an alkaline pre-treat solution slug substantially into the entire vertical thickness of the oil column

23. A method of claim 22 wherein the alkaline pre-treat solution slug comprises an aqueous solution of sodium carbonate or sodium orthosilicate.

24. A method of claim 21 wherein the drive fluid is a field brine, fresh water or a mixture thereof of salinity lower than necessary to produce a Type III phase environment for the surfactant/brine/oil system of the reservoir

25. A method of claim 23 wherein the drive fluid is a field brine, fresh water or a mixture thereof of salinity lower than necessary to produce a Type III phase envi-

ronment for the surfactant/brine/oil system of the reservoir

26. A method of claim 24 wherein the salinity of the pre-flush slug is about 0.4 to about 2.0%

27. A method of claim 26 wherein the salinity of the surfactant slug is about 0.4 to about 2.0%

28. A method of claim 27 wherein the salinity of the slug of the mobility control polymer is about 0.2 to about 1.0%

29. A method of claim 25 wherein the salinity of the pre-flush slug is about 0.4 to about 2.0%

30. A method of claim 29 wherein the salinity of the surfactant slug is about 0.4 to about 2.0%

31. A method of claim 30 wherein the salinity of the slug of the mobility control polymer is about 0.2 to about 1.0%

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United States Patent [19]
Durand et al.

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[54] **PROCESS FOR MANUFACTURING
INVERSE MICROLATICES OF
WATERSOLUBLE COPOLYMERS, THE
RESULTANT INVERSE MICROLATICES
AND THEIR USE FOR IMPROVING THE
PRODUCTION OF HYDROCARBONS**

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524/831**

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[56] **References Cited**

U S PATENT DOCUMENTS

Re. 28,474 7/1974 Anderson et al .. 523/336
3 284,393 11/1966 Vanderhoff et al .. 526/207
3 826,771 7/1974 Anderson et al. .. 524/817
4,021 399 5/1977 Hunter et al - - - 524/827
4,022 731 5/1977 Schmitt .. - - - - 524/166
4,070,321 1/1978 Goretta et al .. 524/829
4,077 930 3/1978 Lam et al .. - - - 524/829
4,147,681 4/1979 Lam et al .. - - - 524/831

4,242,247 12/1980 Pellon et al 260/29 6
4 330,450 5/1982 Lipowski et al .. 524/547
4 435,528 3/1984 Domina .. 524/827
4,464,508 8/1984 Easterly, Jr .. 524/801
4,521,317 6/1985 Candau et al .. 252/8 55 D
4,524,175 6/1985 Stanley, Jr .. 524/831

FOREIGN PATENT DOCUMENTS

0074661 3/1983 European Pat. Off .. 524/831
0119078 9/1984 European Pat. Off 524/831
2354006 5/1975 Fed Rep of Germany
0841127 7/1960 United Kingdom 524/801
2093464 9/1982 United Kingdom .. 524/827
2118200 10/1983 United Kingdom .. 524/827
2140433 11/1984 United Kingdom .. 524/831

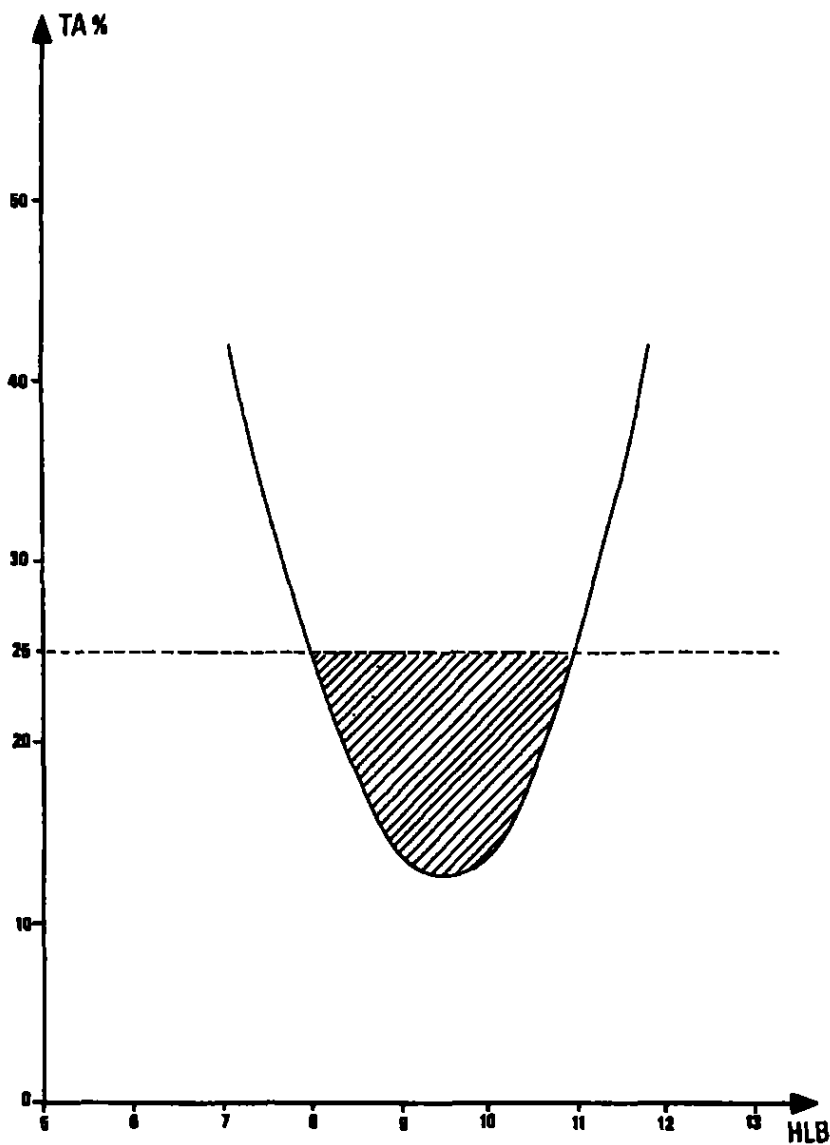
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[57] **ABSTRACT**

By a new process, inverse microlatices of watersoluble copolymers are prepared by copolymerization within an inverse microemulsion obtained by admixing an aqueous phase containing the hydrosoluble monomers to be copolymerized, an organic phase and a non-ionic surfactant or a mixture of non-ionic surfactants, whose H L B ranges from 8 to 11

The resultant microlatices can be diluted in water so as to form thickened solutions, which can be used to improve the production of hydrocarbons from oil formations, particularly in enhanced recovery methods or methods for preventing water inflows in producing wells.

13 Claims, 1 Drawing Figure



PROCESS FOR MANUFACTURING INVERSE MICROLATICES OF WATERSOLUBLE COPOLYMERS, THE RESULTANT INVERSE MICROLATICES AND THEIR USE FOR IMPROVING THE PRODUCTION OF HYDROCARBONS

The invention relates to a process for manufacturing inverse microlatices by copolymerization, in an inverse microemulsion, of at least two hydrosoluble vinyl monomers, and to the inverse microlatices obtained by this process by "hydro-soluble" is meant "water-soluble" throughout

It also concerns the use of these inverse microlatices in the preparation of thickened aqueous solutions for improving the production of hydrocarbons

BACKGROUND OF THE INVENTION

The energy crisis has led to the development of numerous surveys in order to recover a maximum amount of the oil present in the fields. Among the various considered methods, one of them consists of flooding the oil field by means of an injection of salt water in order to force petroleum out of the pores of the rock where it is adsorbed. However, the difference in mobility between oil and water considerably reduces the efficiency of said method. In order to improve this technique, it is known to thicken the injection water by means of hydrosoluble polymers, such as partially hydrolized polyacrylamides, acrylamide-sodium acrylate copolymers or polyaccharides

On the other hand, it has been found that aqueous solutions, thickened by means of polymers, injected in wells simultaneously producing water and oil, limit the water production sufficiently without changing the oil production. However, the use of hydrosoluble polymers under actual conditions of use on the field, is often a delicate operation. As a matter of fact, the handling, storing and dissolution of polyacrylamides, as powder, gives rise to certain problems, particularly those due to absorption of moisture causing, formation of agglomerates, whose dissolution is time-consuming

For this reason, new modes of conditioning hydrosoluble polymers have been proposed, particularly with inverse latices offering as a rule, all the advantages associated with liquids handling. In this connection U.S. Pat. Nos. 3,284,393, 3,624,019, 3,826,771 and 4,022,731, as well as German patent application No. DE-A-2,554,082 and British Pat. No. 2,030,578, are of particular interest.

In the formulations disclosed in these documents, the surfactant is most often selected from non-ionic surfactants having a low H L B (Hydrophilic Lipophilic Balance), providing a water-in-oil emulsion. It consists usually of a sorbitan monooleate or monostearate. On the other hand, it has been stated that certain surfactants of higher H L B are also liable to give water-in-oil emulsions (French Pat. No. 2 245 671)

However, inverse latices obtained according to the prior art methods suffer from different disadvantages, particularly an instability which results in a strong tendency to settle and in the requirement of intense and delicate shearing during their dissolution in aqueous phase, i.e. during their inversion.

More recently, it has been proposed to use inverse microlatices of hydrosoluble polymers of improved stability (French patent application No. 2 524 895),

prepared by using anionic or cationic surface-active agents.

SUMMARY OF THE INVENTION

A new process for preparing stable, transparent inverse microlatices, of hydrosoluble copolymers, using certain proportions of non-ionic surfactants and resulting in increased contents of copolymers, has now been discovered. This is of particular interest in view of the use of these microlatices to form thickened solutions used for improving the production of oil fields

The microlatices prepared by the process of the invention further have the advantage of being auto-invertible.

The process for manufacturing inverse microlatices according to the invention is generally defined by the following steps of

(a) preparing a microemulsion (stable and transparent) of the water-in-oil type, by admixing

(i) an aqueous solution of the acrylic monomers to be copolymerized with

(ii) an oily phase, comprising at least one hydrocarbon liquid,

(iii) in the presence of at least one non-ionic surfactant whose H L B value ranges from 8 to 11 (when using a mixture of surfactants, the resultant H L B is considered).

(b) subjecting the obtained inverse microemulsion of step (a) to polymerization conditions up to complete polymerization and production of a stable, transparent, inverse microlatex of high molecular weight (the term transparent also meaning translucent)

It will be recalled that an emulsion is a biphasic, turbid, unstable medium. Under stirring, particles, dispersed either in water or in oil, are observed which have a wide size distribution about an average value of the order of a micron. When polymerizing an emulsion, the polymer is dispersed in the large emulsion drops (diameter of about 1 to 10 microns) as well as in the small emulsifier micelles (diameter of about 5 to 10 nm).

A microemulsion is also formed of two liquids insoluble in each other and a surfactant, but, in contrast with the emulsion, the mere mixture of the constituents gives, without any agitation, a transparent or translucent thermodynamically stable medium

In the formulations of inverse microemulsions leading to the microlatices of the invention, the aqueous phase contains at least two hydrosoluble acrylic monomers on the one hand, acrylamide and/or methacrylamide and, on the other hand, at least another acrylic monomer selected from acryic acid, methacrylic acid and alkali salts of these acids. In the mixture of acrylic monomers, the second acrylic monomer content may range from 15 to 60% by weight and preferably from 20 to 45% by weight.

In order to obtain an inverse microemulsion, it is generally necessary to use particular conditions whose main parameters are as follows: surfactant concentration, H L B of the surfactant or of the surfactant mixture, temperature, nature of the organic phase and composition of the aqueous phase.

The monomers content of the aqueous phase is generally 20-80% and usually 30-70% by weight.

Generally the pH of the monomers aqueous solution ranges from 8 to 13 and advantageously from 9 to 11

The selection of the organic phase has a substantial effect on the minimum surfactant concentration necessary to obtain the inverse microemulsion. This organic

phase may consist of a hydrocarbon or a hydrocarbons mixture. Isoparaffinic hydrocarbons or mixtures thereof are the best suitable in order to obtain inexpensive formulations (lower content of surfactants) of inverse microemulsions.

The ratio by weight of the amounts of aqueous phase and hydrocarbon phase is chosen as high as possible, so as to obtain, after copolymerization, a microlatex of high copolymer content. Practically, this ratio may range, for example, from 0.5 to 3/1, usually it is close to 2/1.

The one or more surfactants are selected in view to obtain a H L B value ranging from 8 to 11. As a matter of fact, outside this range, the inverse microemulsions either cannot be obtained, or require a considerable amount of surfactants, incompatible with an economical process. In addition, in the so-defined H L B range, the surfactant content must be sufficient to obtain an inverse microemulsion. Too low concentrations of surfactants lead to inverse emulsions similar to those of the prior art and form no part of this invention.

Within the H L B range, the surfactant concentration, in proportion to all of the constituents of the microemulsion is preferably higher than a value y (in % by weight) approximately defined by the following empirically determined equation:

$$y = 1.8x^2 - 110x + 534$$

wherein x is the H L B value of the surfactant or surfactant mixture.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawing shows a curve representing the surfactant concentration versus the H L B value. On this figure, the preferred domain of the invention has been hachured.

With respect to the upper limit of the surfactant concentration, it is desirable, for economical reasons, to limit said concentration to 25% by weight of all the constituents of the inverse microemulsion.

When preparing the inverse microemulsion, the temperature of the mixture must be carefully controlled, in view of the sensitivity to temperature of the inverse microemulsions in the presence of non-ionic surfactants. This temperature influence is increased as the surfactant concentration is closer to the minimum content required for obtaining an inverse microemulsion.

In order to reduce the required surfactant content, and to limit to a minimum the temperature influence on the stability of the inverse microemulsions, the latter will be, as much as possible, prepared at a temperature as close as possible to that selected for the copolymerization.

The hydrosoluble acrylic monomers present in the above-described inverse microemulsion are polymerized photochemically or thermally: the method consists of photochemically initiating the copolymerization, for example by ultraviolet radiation or thermally by means of a free radical generator, either hydrophobic, such as, for example, azobisisobutyronitrile, or hydrophilic, such, for example, as potassium persulfate.

The copolymerization is performed very quickly, for example in a few minutes, in a photochemical way, quantitatively, and leads to the formation of stable and transparent microlatexes whose particles radius is of the order of 20-40 nanometers with a narrow distribution range.

The size of the particles dispersed in the inverse microlatexes according to the invention may be determined by means of the quasi-elastic light scattering. The optical source on the light scattering apparatus consists of a Spectra Physica argon-ion laser operating at 488 nm. The time dependant correlation function of the scattered intensity is derived by using a digital correlator with 72 channels. The intensity correlation data have been treated by using the method of cumulants, giving the average decay rate $\langle \Gamma^{-1} \rangle$ of the correlation function and the variance V . The latter measures the amplitude of the distribution of the decay rate and its value is given by the formula:

$$V = (\langle \Gamma \rangle^2 \langle \Gamma^2 \rangle) / \langle \Gamma \rangle^2$$

wherein $\langle \Gamma^2 \rangle$ is the second moment of the distribution.

For copolymer solutions of low polydispersity, the variance V , as a first approximation, is related to the polydispersity index M_w/M_n (weight average molecular weight/number average molecular weight) by the relationship:

$$M_w/M_n = 1 + 4V$$

The molecular weight of the obtained copolymers depends to a large extent on the copolymerization temperature. Temperatures lower or equal to about 30° C. are always preferred when very high molecular weights are desired, as for inverse microlatexes destined to be used in Enhanced Oil Recovery.

The process of the invention provides stable and transparent inverse microlatexes of high hydrosoluble copolymer content (20 to 35% by weight). The inverse microlatexes, prepared in the presence of non-ionic surfactants, have a remarkable stability to temperature in contrast with the inverse microemulsions from which they are prepared.

Inverse microlatexes obtained by the process of the invention, can be used in many applications, particularly in the techniques of oil production. Hydrocarbons Enhanced Recovery, ground consolidation, manufacture of drilling muds, prevention of water inflows during the bringing in production of oil wells, and as completion or fracturation fluids.

Generally, the Enhanced Oil Recovery methods with the use of polymer aqueous solutions consist of injecting said solutions in the field through at least one injection well, to circulate it through the formation and recover the displaced hydrocarbons through at least one producing well.

The methods using inverse microlatexes of the invention for Enhanced Recovery are not substantially different from those above-described for the water-in-oil emulsions. The inverse microlatexes considered in this invention are auto-invertible and it is not necessary generally to add an additional surfactant to favor the inversion, as in certain above-described methods. These microlatexes are used, for example after dilution in water, in a proportion on of 50 to 5000 ppm, preferably 100 to 2000 ppm by weight of copolymer with respect to the resultant aqueous phase. Tests conducted in laboratory have shown the efficiency of the inverse microlatexes used.

The method for preventing water inflows in producing wells, consists of injecting into the producing well, in the part of the field to be treated, an aqueous solution

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of polymer, prepared according to the invention by inverse microlatex dissolution in water. The polymer is adsorbed to a large extent on the walls of the formation surrounding the well where it is injected. When and well is then brought again in production, the oil and/or the gas selectively traverse the treated zone whereas the water passage is reduced.

In addition to these applications, the hydrosoluble polymers, prepared as a microemulsion, may be used as coagulants for separating solids suspended in liquids, floatation and draining adjuvants in the manufacture of paper pulp; or

floculants in water treatment.

The inverse microlatexes obtained by the process of the invention may also be used in assembling of glass fibers, in the leather industry or in the field of paints.

EXAMPLES

The following examples illustrate the invention, but must not be considered as limiting in any way the scope thereof. Examples 1, 10 and 14 to 17 are given by way of comparison and form no part of the invention.

EXAMPLE 1 (comparative)

77.8 g of SOLTROL 220 (inorganic paraffinic oil having a distillation point of 244° C. and a final point of 287° C.), 25 g of a mixture of 21.4 g of polyoxyethylene sorbitol hexaoleate (ATLAS G 1086) and 3.6 g of sorbitan sesquileste (ARLACEL 83) whose HLB (hydrophobic lipophilic balance) is 9.25, are admixed under stirring. 61.3 g of acrylamide and 20.7 g of glacial acrylic acid are dissolved in a mixture of 42.2 g of distilled water with 23.0 g of a 50% by weight sodium hydroxide solution and this solution is added to the oil/surfactant mixture. The amount of surfactants corresponds to 10% by weight of all the constituents. After one hour of purging with nitrogen at room temperature, the resultant emulsion (turbid and unstable) is heated to 40° C. and 6.5 10⁻⁴ mole of t-butyl peroxyprvalate per mole of monomer are added thereto, the temperature being maintained between 40° and 50° C. for about 1 hour.

The so-obtained latex is turbid and decantation takes place during storage.

EXAMPLE 2

When example 1 is repeated, but with the use of 63.5 g of surfactants mixture, which corresponds to 22% by weight of all the constituents, the resultant mixture, in contrast to example 1, is limpid and monophasic (microemulsion) and remains as such after copolymerization. By precipitation in acetone and successive washings with acetone and methanol, an acrylamide-sodium acrylate copolymer is obtained. Its viscosity in aqueous solution (400 ppm of copolymer and 5000 ppm of NaCl), measured at 30° C., is 1.30 mm²/s.

EXAMPLE 3

Example 1 is repeated but as the organic solvent an isoparaffinic cut (ISOPAR M) having an initial distillation point of 207° C. and a final point of 254° C. is used and a mixture of surfactants (36.6 g) corresponding to 14% of the weight of all the constituents is used. The resultant mixture is limpid and monophasic.

After copolymerization, a monophasic mixture (microlatex) containing 33.3% by weight of acrylamide-sodium acrylate copolymer is obtained. An aqueous solution containing 400 ppm of said copolymer and

5000 ppm of NaCl, measured at 30° C. has a viscosity of 1.4 mm²/s.

EXAMPLE 4

255 g of ISOPAR M and 90 g of a mixture of surfactants consisting of 12.6 g of sorbitan sesquileste and 77.4 g of polyoxyethylene sorbitol hexaoleate (resultant HLB 9.3) are added to an aqueous solution containing 38.25 g of acrylic acid and 89.25 g of acrylamide neutralized with sodium hydroxide to a pH close to 10. This amount corresponds to 15% by weight of all the constituents. 0.21 g of azobisisobutyronitrile is added to the resultant monophasic mixture which is degased for 1 hour and heated for 2 hours at 60° C., giving a stable and transparent microlatex whose particle radius, determined by quasi-elastic light scattering, is about 25nm, with a variance of 3%.

By precipitation in acetone and successive washings with acetone and methanol, an acrylamide-sodium acrylate copolymer is obtained (with a total conversion) whose viscosity, determined at 30° C. in a 400 ppm copolymer and 5000 ppm NaCl aqueous solution, is 1.5 mm²/s.

EXAMPLE 5

Example 4 is repeated, except that azobisisobutyronitrile is omitted and the copolymerization is conducted under UV radiation for 5 minutes, the temperature being maintained at 20° C. With a total conversion, an acrylamide-sodium acrylate copolymer is obtained whose viscosity, measured at 30° C. in a 400 ppm copolymer and 5000 ppm NaCl aqueous solution, is 3.15 mm²/s. On the other hand, the intrinsic viscosity of said copolymer, dissolved in water containing 20 g/l of NaCl, has been found equal to 3250 cc/g on the basis of measurements effected with a LS 30 viscosimeter of CONTRAVES Company and extrapolated to zero concentration and shear rate.

EXAMPLE 6

In the conditions of example 4 for carrying out the inverse microemulsion, the proportions of each of the two surfactants are varied and the minimum amount of surfactants for obtaining, after copolymerization, a stable and transparent inverse microlatex, is determined in each case.

The results are reported in the following table.

TABLE I

Minimum surfactant concentration to obtain a stable and transparent inverse microlatex (% by weight)	
HLB	
8.5	18
9	14
9.5	12
10.2	16

EXAMPLE 7

200 g of ISOPAR M and 92 g of the surfactant mixture of example 5 are added to 400 g of an aqueous solution containing 60 g of acrylic acid, 140 g of acrylamide and the sodium hydroxide amount required to attain a pH close to 10. This amount corresponds to 13.3% by weight of all the constituents. The copolymerization, conducted under the same conditions as described in example 5, provides a stable and transparent microlatex whose particles radius, determined by

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quasi-elastic light scattering, is about 40 nm, with a variance of 5%. This inverse microlatex contains 31.6% by weight of an acrylamide-sodium acrylate copolymer containing 35.9% by weight of sodium acrylate.

The intrinsic viscosity of said polymer is 3520 cc/g (solution at 20 g/l of NaCl).

EXAMPLE 8

200 g of ISOPAR M and 106 g of the mixture of surfactants of example 4 are added to 400 g of an aqueous solution containing 40 g of acrylic acid, 160 g of acrylamide and the sodium hydroxide amount required to attain a pH of 9. This amount corresponds to 15% by weight of all the constituents. The copolymerization, conducted in the same conditions as in example 5, gives a monophasic mixture containing 30.1% by weight of acrylamide-sodium acrylate copolymer containing 24.6% by weight of sodium acrylate.

The viscosity of an aqueous solution containing 400 ppm of said copolymer, determined at 30° C. in the presence of 5 g/l of NaCl, is 2.7 mm²/s.

EXAMPLE 9

When, in example 8, ISOPAR M is replaced with trimethyl-pentane, everything else being unchanged, an inverse microlatex of similar characteristics as in example 8 is obtained.

EXAMPLE 10 (comparative)

When, in example 8, the isoparaffinic solvent (ISOPAR M) is replaced with an aromatic solvent (toluene), everything else being unchanged, it is impossible to obtain an inverse microemulsion, even with the addition of high amounts of surfactants (31% by weight).

EXAMPLE 11

200 g of ISOPAR M and 115 g of a mixture of surfactants containing 11% by weight of sorbitan trioleate (Montane 85) and 89% by weight of ethoxylated sorbitan trioleate (Montanox 85) are added to 400 g of an aqueous solution containing 60 g of acrylic acid and 140 g of acrylamide, whose pH has been brought to 10 by addition of sodium hydroxide. The H L B of the surfactants mixture is 10 and the surfactant amount corresponds to 16% by weight of all the constituents.

The copolymerization, conducted in the same conditions as described in example 5, gives a monophasic mixture containing 30.5% by weight of an acrylamide-sodium acrylate copolymer containing 35.9% by weight of sodium acrylate.

The intrinsic viscosity of said polymer is 3200 cc/g (in aqueous solution at 20 g/l of NaCl).

EXAMPLE 12

200 g of ISOPAR M and 115 g of the mixture of surfactants of example 11 are added to 400 g of an aqueous solution containing 170 g of acrylamide and 30 g of acrylic acid, whose pH has been brought to 9 by addition of sodium hydroxide. This amount corresponds to 16% by weight of all the constituents.

The copolymerization, achieved in the same conditions as in example 5, gives a monophasic mixture containing 29.3% by weight of an acrylamide-sodium acrylate copolymer containing 18.7% by weight of sodium acrylate.

EXAMPLE 13

200 g of ISOPAR M and 100 g of polyoxyethylene sorbitol oleate (ATLAS G 1087, H L B=9.2) are added to 400 g of an aqueous solution containing 50 g of acrylic acid and 150 g of acrylamide, whose pH has been brought to 10 by addition of sodium hydroxide. This amount corresponds to 14.3% by weight of all the constituents.

The copolymerization so-obtained copolymerization of the inverse microemulsion, conducted in the conditions described in example 5, gives a stable and transparent inverse microlatex containing 30.7% by weight of an acrylamide-sodium acrylate copolymer containing 30.3% by weight of sodium acrylate.

EXAMPLE 14 (comparative)

When example 7 is repeated, except that the proportions of the two surfactants are modified so as to obtain the resultant H L B of 7.6, it is not possible to obtain, under these conditions, any inverse microemulsion, even when adding high amounts of surfactants (more than 31% by weight).

EXAMPLE 15 (comparative)

When, in example 7, the mixture of surfactants is replaced with ethoxynonylphenol containing 8 ethylene oxide recurrent units per molecule and having a H L B of 12.3, everything else being unchanged, it is not possible to obtain in these conditions, any inverse microemulsion, even when adding high surfactant amounts (more than 35% by weight).

EXAMPLE 16 to 22

255 g of ISOPAR M and a variable amount of a mixture of surfactants having a H L B value of 9.3, already used in certain of the preceding examples (14% by weight of sorbitan sesquioleate and 86% by weight of polyethoxylated sorbitol hexaoleate) are added to 255 g of an aqueous solution containing 44 g of acrylic acid and 82 g of acrylamide, neutralized with sodium hydroxide up to a pH close to 10. The amount of surfactant mixture is reported in table II hereinafter. The resultant mixture is degassed and then heated at 45° C. for 45 minutes in order to copolymerize the monomers.

There is thus obtained a series of inverse latices whose final copolymer concentration is about 22 to 25% by weight with respect to all the constituents. The proportion of sodium acrylate in the copolymers is 42% by weight. Table II hereinafter reports, for the final latices, the values of optical transmission measured by turbidimetry, the hydrodynamic radii R_H of the particles, determined by the quasi-elastic diffusion of light and an evaluation of the stability of said latices.

TABLE II

Ex- am- ples	Surfactant concentration (% by weight)	Optical transmission (%)	R_H (nm)	Stability
16*	8.2	11	> 89	Sedimentation after a few hours
17*	11.0	1.2	> 60	
18	13.4	82	37	Stable
19	15.5	82	35	even
20	18.0	85	27.5	after
21	20.2	88	25	several
22	21.1	91	24	months

*comparative examples

From this table, it appears that microlatexes obtained in examples 18 to 22 are stable and have a high optical transmission and a small particle radius, in contrast with the results obtained in examples 16 and 17

The values of surfactants or surfactant mixtures concentrations, taking into account the corresponding H L B values, were used to draw a curve shown in the accompanying FIGURE, indicating the approximate limit between a zone wherein no stable inverse microlatex is obtained and a zone wherein stable inverse microlatexes can be obtained. On this FIGURE, the preferred domain of the invention has been hachured

EXAMPLES 23 to 25

100 g of ISOPAR M and 53 g of the same surfactant mixture as in the preceding examples (H L B=9.3) are added to 200 g of an aqueous solution containing 30 g of acrylic acid and 70 g of acrylamide, neutralized with sodium hydroxide up to a pH close to 9

The obtained monophasic mixture, to which is added 0.15 g of azobisisobutyronitrile, is degased and maintained for 5 hours at a temperature differing according to the considered example. A stable and transparent inverse microlatex is always obtained and the copolymerization is complete.

By precipitation in acetone and successive washings with acetone and methanol, acrylamide-sodium acrylate copolymers are separated and their viscosity determined, at 30° C., in aqueous solutions containing 1000 ppm of copolymer and 5000 ppm of sodium chloride. The viscosity values are different according to the copolymerization temperature

Example 23	T° = 60° C.	Viscosity: 2.4 mm ² /s
Example 24	T° = 40° C.	Viscosity: 4.9 mm ² /s
Example 25	T° = 25° C.	Viscosity: 7.4 mm ² /s

EXAMPLE 26

Test of injectivity of porous medium

A porous medium is prepared by packing, in a glass cylinder, sand from ENTRAIGUES EN 38, of granulometry ranging from 28 to 50 µm. The characteristics of the so-obtained porous medium are as follows: L=60 mm, Φ=20 mm, Vp=86 cc, k=2.04 D, φ=45% (k=permeability to water expressed in Darcy, φ=porosity)

A solution of acrylamide-sodium acrylate copolymer (1000 ppm) is prepared by dispersing the inverse microlatex obtained in example 7 in a field brine of total salt content close to 3 g/l. The rheological curve of said copolymer solution, as determined by means of LS 30 viscosimeter, makes apparent the presence of a plateau in the values of relative viscosity versus shear rate (relative viscosity at zero shear rate: ηR₀=20, at 30° C.)

The polymer solution is then injected at constant rate (q=15 cc/h by means of a piston pump of perfuser type; the pressure losses are measured at the terminals of the porous medium for the polymer solution and expressed in proportion to the values initially obtained with the field brine. Thus, a mobility ratio is defined which, in the experimental conditions, becomes stabilized at a value of 21.6. It is further observed that the stabilization of the mobility decrease corresponds to an equalization of the polymer concentrations, determined by viscosimetry, between the input and the output of the core. The comparison of the mobility decrease val-

ues with the plateau viscosity on the one hand, and the absence of polymer losses between the input and the output of the porous medium on the other hand, shows that for the selected porous medium, the injectivity of the microlatex dispersion is satisfactory. Particularly, no indication of clogging was observed

When injecting field brine after the polymer solution, a value of the permeability reduction of 2.36 is obtained, which characterizes the presence of an adsorbed polymer layer on the walls of the porous medium. This behavior is characteristic of an acrylamide-sodium acrylate copolymer of high molecular weight.

On the other hand, the fact that the permeability to water is permanently reduced makes it possible to contemplate the use of the inverse microlatexes of the invention in the prevention of water inflows in producing wells, as illustrated in the following example.

EXAMPLE 27

A porous medium (L=20 cm, Φ=5 cm) is prepared by coring a Vosges sandstone containing about 10% of clay. The permeabilities of this Vosges sandstone to sea water (total salt content ≈37 g/l and to the field water (total salt content ≈8 g/l) are respectively 0.478 D and 0.467 D. The porosity is 18%

From the microlatex of example 13, a solution is separately prepared which contains 500 ppm of active copolymer in sea water and in field water. The relative viscosities obtained in the Newtonian zone of said microlatex dispersed in both water types are respectively ηR₀=5.1 (field water) and ηR₀=3.1 (sea water), the ratio of the two viscosities being equal to 1.65

In conformity with the teaching of the French Pat. No. 2 325 797 (corresponding to U.S. Pat. No. 4,095,651) issued to the name of the applicant and concerning the prevention of water inflows in producing wells, the microlatex solution (Cp=500 ppm) is injected at constant rate q=3 cm³/h (γ=2.1 sec⁻¹) in sea water (t=30° C.). After injection of about 5 Pv (Pv=pores volume) of said microlatex solution, the polymer injection is discontinued and sea water is injected by the inlet face of the core in view to determine, on the one hand, the decrease of permeability R_k to sea water before and after the polymer introduction and, on the other hand, to deduce therefrom a thickness of the adsorbed layer, calculated by the formula

$$\delta = R_p \left(1 - \frac{1}{\sqrt{\frac{\eta R_0}{\eta R_k}}} \right)$$

wherein R_p designating the average pore radius is equal to

$$\sqrt{\frac{R_k}{\gamma}}$$

The obtained values are as follows: R_k=1.80, δ=0.62 µm

Through the outlet face of the core, field water is injected in opposite direction, thus simulating the water production in the producing well. New values of the permeability reduction and of the thickness of the adsorbed layer are thus respectively obtained: R_k=2.92, δ=0.90 micron. The ratio of the respective thicknesses of adsorbed layers respectively with the field water and

the sea water is 1.61, value which is very close to 1.65, representing the ratio of the plateau viscosities in said two waters. This indicates that the introduction of the copolymer took place in such conditions that the thickness of the adsorbed layer varied in the same ratio as the viscosities. Accordingly, the production of soft water from the field is decreased, thereby decreasing the production water/oil ratio (WOR).

What is claimed as the invention is.

1 A process for producing a stable inverse microlatex comprising the steps of

(a) admixing

an aqueous solution containing at least one acrylic monomer (i) selected from acrylamide and methacrylamide and at least another acrylic monomer (ii) selected from acrylic acid, methacrylic acid and alkali salts of said acids, at a concentration from 20 to 80% by weight in said aqueous solution,

an oily phase comprising at least one hydrocarbon liquid, the ratio by weight between said aqueous solution and said oily phase being from 0.5/1 to 3/1, and

a non-ionic surfactant or a non-ionic surfactant mixture having a H.L.B. from 8 to 11, in a proportion, with respect to all the involved constituents, higher than about a value y , given, in percent by weight, by the relationship:

$$y = 5.8 X^2 - 110 X + 534$$

wherein X is the H.L.B. of said surfactant or said surfactant mixture, so as to form an inverse microemulsion, and

(b) subjecting the inverse microemulsion obtained in step (a) to copolymerization conditions.

2 A process according to claim 1, wherein said acrylic monomer (ii) is sodium acrylate.

3 A process according to claim 1, wherein said acrylic monomer (ii) amounts to 15-60% by weight of the acrylic monomer mixture

4 A process according to claim 3, wherein said acrylic monomer (ii) amounts to 20-45% by weight of the acrylic monomer mixture.

5 A process according to claim 1, wherein, in step (a), the pH of said aqueous solution is from 8 to 13

6 A process according to claim 1, wherein, in step (a), the oily phase comprises at least one isoparaffinic hydrocarbon

7 A process according to claim 1, wherein, in step (a), the ratio by weight between the monomers aqueous solution and the oily phase is about 2/1

8 A process according to claim 1, wherein, in step (a), the proportion of surfactant or surfactant mixture is at most 25% by weight of all the constituents of said inverse microemulsion

9 A process according to claim 1, wherein, in step (b), the polymerization is conducted by heating in the presence of a radical reactions initiator

10 A process according to claim 1, wherein, in step (b) the polymerization is initiated by radiation.

11 An inverse microlatex obtained by the process according to claim 1 having a copolymer content from 20 to 35% by weight.

12 In a method for preparing a thickened aqueous solution, comprising diluting in water an inverse microlatex in such a proportion that the resultant aqueous solution has a copolymer concentration from 50 to 5000 ppm by weight the improvement wherein the inverse microlatex is one of claim 11

13 A thickened aqueous solution, obtained by the method of claim 12.

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United States Patent [19]

Hayes et al.

[11] 4,012,329

[45] Mar. 15, 1977

[54] WATER-IN-OIL MICROEMULSION
DRILLING FLUIDS

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1973 abandoned

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252/308, 252/309

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[58] Field of Search 252/8.5 M, 8.5 P, 308,
252/309, 166/273, 274, 275, 175/65

[56] References Cited

UNITED STATES PATENTS

2,696,468	12/1954	Fischer	252/8.5 M
2,739,120	3/1956	Fischer	252/8.5 M
3,002,923	10/1961	Barker et al.	252/8.5 P

3,111,491	11/1963	Atkins	252/8.5 M
3,252,903	5/1966	Crittendon	252/8.5 P
3,254,714	6/1966	Gogarty et al.	166/275
3,330,343	7/1967	Toach et al.	166/275
3,734,856	5/1973	Son	252/8.5 M

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[57] ABSTRACT

An oil-external microemulsion drilling fluid having a wide range of tolerance for salinity, having good gel strength and low fluid loss characteristics, and also obtained by mixing about 1% to about 30% of a sodium petroleum sulfonate having an average equivalent weight within the range of about 350 to about 525, about 5% to about 84% of a hydrocarbon (e.g. diesel fuel), about 15% to about 90% of an aqueous medium (can contain water soluble salts), about 0.01 to about 20% of a cosurfactant (e.g. alcohols such as primary amyl alcohol) and about 0.1 to about 15% of bentonite clay. Weighting agents, e.g. barite, and other desired additives can be added to the microemulsion.

24 Claims, No Drawings

WATER-IN-OIL MICROEMULSION DRILLING FLUIDS

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of our copending patent application, Ser No 391,109, filed Aug. 27, 1973, now abandoned.

BACKGROUND OF THE INVENTION

1 Field of the Invention

This invention defines a composition useful as a drilling fluid. The composition is an oil-external microemulsion containing sodium petroleum sulfonate, water, hydrocarbon, bentonite, and optionally, cosurfactant.

2 Description of the Prior Art

Drilling fluids desirably have a variety of characteristics to facilitate exploitation of hydrocarbons in subterranean reservoirs. For example, the drilling fluid desirably lubricates and cools the drill string and bit during drilling operations, supports to some degree the weight of drill string and casing, prevents the sticking of drill pipe while in the borehole, keeps cuttings in suspension, carries the cuttings from the bit to the surface, releases the cuttings and any gas in the drilling fluid at the surface, provides well bore stability, prevents fluid from entering reservoir formations (i.e. prevents fluid loss), prevents formation fluids (oil, gas, water) from entering the well bore, provides corrosion protection, controls formation pressures, and aids in well-logging techniques (e.g. conducts electrical current needed for conventional electrical logging), etc. To perform the above functions, it is desired that the drilling fluid should.

- 1 have sufficient viscosity to support and transport cuttings and weighting materials,
- 2 be fluid and pumpable,
- 3 have sufficient gel strength to support cuttings and weighting materials when circulation stops,
- 4 be stable at a wide range of pressures, temperatures, and shear rates,
- 5 have the property to build filter cakes on the formation to prevent fluid loss,
- 6 be chemically flexible so that the pH, etc. of the drilling fluid can be controlled, and
- 7 conduct electrical current. The prior art does not know of a drilling fluid that will effectively meet all of the above requirements.

Four basic types of drilling fluids are presently available to the industry:

- 1 Water-based mud which is the most common and which consists of water (fresh or salt), various clays, weighting materials, and other necessary additives;
- 2 Oil-in-water emulsion muds generally composed of an emulsifier, oil, and water and other additives,
- 3 Oil-based muds which contain refined hydrocarbons, e.g. diesel oil, a few percent water, and additives, and
- 4 Water-in-oil emulsion muds which are often called inverted emulsion muds and consist of emulsifiers, water and oil, and other additives. The water-in-oil emulsion muds are the most popular for overcoming most of the serious drilling problems. A typical oil-external emulsion mud consists of diesel oil and water in a 7:3, 6:4, or 5:5 ratio to which may be

added (1) gelling and suspending agents such as clay-organo complexes, (2) emulsifiers such as anionic, sodium, and calcium salts of fatty acids, or cationic amine derivatives which supposedly are stable at high temperatures and in the presence of salt; (3) oil-wetting agents such as organic phosphates; and (4) filtration control agents such as clays or non-asphaltic organic colloids. The water-in-oil emulsion muds can be used as drilling fluids, completion fluids, or workover fluids and are generally preferred over water-based muds since the latter may cause problems with water-sensitive reservoirs. However, the water-in-oil emulsion muds are generally more expensive than the water-based muds. This added expense is generally justified to

- 1 prevent formation damage to water-sensitive reservoirs,
- 2 maintain hole stability in heaving, dispersing, swelling, sticky, and sloughing shales by shielding the shales from free water;
- 3 prevent hole enlargement and permit coring in water-soluble rocks, such as salt,
- 4 secure full core recovery in unconsolidated formations,
- 5 obtain cores which have not been flushed by water filtrate,
- 6 maintain stable mud properties in deep and high temperature holes which require heavy mud,
- 7 prevent differential-pressure sticking of drill pipe,
- 8 prevent corrosion of drill pipe, casing, and tubing which reduces expensive workovers,
- 9 permit the use of aluminum drill pipe for deeper drilling by protecting aluminum from salt corrosion,
- 10 increase drilling rates by better lubrication and removal of shale cuttings without disintegration of cuttings, and
- 11 generally permit the obtaining of lower density drilling fluids than water-based muds. Another advantage with the water-in-oil emulsion muds is that they generally can be reclaimed for later use, thus reducing the overall cost. Oil-external emulsion muds have found widely accepted use in the Gulf Coast area, Pennsylvania reservoirs of Central Oklahoma, the Arctic North Slope, and reservoirs in Russia. The water-in-oil emulsion muds generally have a high resistivity to electrical current due to the oil, such adversely affects electrical logging techniques.

From a logging standpoint, it is desirable that the drilling fluid be sufficiently conductive of electricity to provide a path for the electric current to pass from the current electrode into the formation. If the fluid is too conductive, short-circuiting can occur between the current and the measuring electrode resulting in a greatly dampened, characterless, and misleading log.

There are many patents teaching examples of drilling fluids. U.S. Pat. No. 2,696,468 to Fischer discloses a conductive oil-base drilling fluid containing up to 10% water, an electrolyte and an emulsifying agent. Fischer teaches that above 10% water the fluid loses its desired properties and becomes an emulsion-base fluid. Fischer in U.S. Pat. No. 2,739,120 teaches similar drilling fluids containing non-ionic surfactants.

U.S. Pat. No. 3,111,491 to Atkins, Jr. et al. teaches that oil-base drilling fluids lose their desired properties when the water concentration exceeds 10%.

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US Pat No 3,110,668 to Anderson teaches an emulsion fluid composed of guar gum derivatives and a surface-active agent (nonionic and cationic) Anderson teaches that emulsions containing anionic surfactants are undesirable unless stabilized in accordance with his invention e.g. in the presence of calcium, magnesium, sodium, and similar materials which are generally encountered during drilling operations

US Pat No 3,264,214 to Stratton teaches the use of metal petroleum sulfonates prepared from high viscosity oils as effective defoaming agents for drilling fluids. The drilling fluid can be an emulsion

SUMMARY OF THE INVENTION

Applicants have discovered an oil-external microemulsion mud which will conduct electrical current (such permits the use of ordinary electrical logging techniques), has suitable viscosity, gel strength, and low fluid loss characteristics, is more economical than conventional water-in-oil emulsion muds, is stable over a wide range of salinity conditions, is inherently corrosion-resistant, has desirable lubricity characteristics, a relatively high water concentration which permits more economical drilling fluids, and which exhibits an unusual characteristic of having more favorable rheological properties as the temperature of the microemulsion increases

DESCRIPTION OF PREFERRED EMBODIMENTS

The water-in-oil microemulsions or oil-external microemulsions contain water, sodium petroleum sulfonate, hydrocarbon, bentonite, and optionally, cosurfactant, electrolyte, gelling agents, fluid loss agents, etc. The water concentration is about 15 to about 90%, preferably about 20 to about 75 and more preferably about 25 to about 50% by volume. The water can optionally contain electrolyte (water-soluble salts). Hydrocarbon is present in volume amounts of about 5 to about 84%, and preferably about 10 to about 78% and more preferably about 25 to about 70%. The sodium sulfonate is present in concentrations of about 1 to about 30% and preferably about 2 to about 20% and more preferably about 5 to about 10% by volume. Concentration of the bentonite is about 0.1 to about 15%, preferably about 1 to about 10% and more preferably about 2 to about 6% by weight. A cosurfactant, also identified as a semi-polar organic compound, can be present in amounts of about 0.01 to about 20% and preferably about 0.1% to about 5% by volume. Electrolytes or water-soluble salts, as mentioned earlier, can be added to the water within the microemulsion, e.g. in amounts of about 0.001 to about 5% and preferably about 0.1 to about 3% by weight, based on the aqueous medium. Other additives can be incorporated into the microemulsion, e.g. additives to impart low fluid loss characteristics.

The hydrocarbon can be crude oil, both sweet and sour, a partially refined fraction of crude oil (e.g. side cuts from crude columns, crude column overheads, gas oils, kerosene, heavy naphthas, naphthas, straight-run gasolins, liquefied petroleum gases), refined fractions of crude oil (propane, butane, pentane, decane, etc.) and synthesized hydrocarbons including halogenated hydrocarbons. From an economical standpoint, the hydrocarbon is preferably a partially refined fraction of crude oil (e.g. diesel fuel or a gasoline cut off of a crude column). Also, unsulfonated hydrocarbon within petroleum sulfonates is useful as the hydrocarbon. Exam-

ples of refined fractions of crude oil or synthesized hydrocarbon include paraffinic compounds such as liquefied petroleum gases, propane, pentane, heptane, decane, dodecane, cycloparaffinic compounds including cyclohexane, etc., aryl compounds including mono as well as polycyclic compounds such as naphthenic and anthracenic compounds and substituted products thereof including toluene, alkyl phenols, etc., halogenated hydrocarbons.

The water can be soft water, brackish water, or brine water. Where a high gel strength is desired, the water is preferably soft or distilled water. Also, where ions are present in the water, it is preferred that the ions are compatible with the ions within the subterranean formation being drilled into.

The petroleum sulfonate useful with Applicants' microemulsions are petroleum sulfonates and more particularly sodium petroleum sulfonates. The average equivalent weight of the sulfonate is within the range of about 350 to about 525, preferably about 400 to about 470 and more preferably about 410 to about 440. The petroleum sulfonate can be a monosulfonate, polysulfonate such as a disulfonate, or mixtures thereof. Also, the petroleum sulfonate can be a pure sulfonate or one having, for example, 50% or more and preferably about 60% or more active sulfonate. The petroleum sulfonate can be a mixture of high, medium, and low average equivalent weight petroleum sulfonates, however, the average equivalent weight of the sulfonate or sulfonates should be within the above indicated ranges.

The cosurfactant can be an alcohol, amine, ester, ether, aldehyde, ketone, or an organic compound containing one or more functional groups identical to the functional groups (e.g. —OH) within the previously mentioned cosurfactant compounds. The cosurfactant contains 1 to about 20 or more carbon atoms and preferably about 3 to about 16 carbon atoms. Preferably, the cosurfactant is an alcohol or an organic compound containing a hydroxyl group and one or more different functional groups, such as an ether group, etc. Examples of preferred cosurfactants include isopropanol, n- and isobutanol, amyl alcohol such as n-amyl alcohol and p-amyl alcohol, 1- and 2-hexanol, 1- and 2-octanol, decyl alcohols, alkaryl alcohols such as p-nonyl phenol and alcoholic liquors such as fusel oil. Mixtures of two or more cosurfactants are useful with this invention.

The electrolytes can be a water-soluble inorganic base, inorganic acid, or inorganic salt, preferably it is the latter. Examples of electrolytes include sodium hydroxide, sodium chloride, sodium sulfate, hydrochloric acid, sulfuric acid, sodium nitrate, ammonium chloride, ammonium hydroxide, potassium chloride, etc. Examples of other useful electrolytes will depend upon the hydrocarbon, aqueous phase, surfactant and cosurfactant, reservoir fluids, reservoir temperature, etc.

The microemulsion can be prepared by dissolving the petroleum sulfonate in the hydrocarbon, then adding water to obtain a desired viscosity. The cosurfactant can optionally be dissolved in the hydrocarbon phase and electrolyte can be dissolved in the water phase. The bentonite is incorporated into the microemulsion by mixing it with the water phase and then combining this bentonite-water sec- with a mixture consisting of the hydrocarbon, petroleum sulfonate, and optional cosurfactant. The amount of water within the microemulsion is directly dependent on the viscosity. Other components

of the microemulsion directly influence the viscosity, e.g. the concentration and type of cosurfactant, the concentration and average equivalent weight of the petroleum sulfonate, the amount of electrolyte within the aqueous phase of the microemulsion, the temperature of the microemulsion, etc.

The microemulsion contains a water-dispersible clay, the dispersibility properties can result from chemical and/or physical properties of the clay. Preferably, the clay has a high degree of hydration, such as bentonite, a clay containing mostly montmorillonite, with minor amounts of quartz, cristobalite, biotite, etc. Other kinds of clays commonly used in drilling fluids may be used in the microemulsion. Examples of useful clays include Aquagel (a trademark of Baroid Division, National Lead Co., Houston, Texas, U.S.A. and identifies a Wyoming bentonite), Baroco (a trademark of Baroid Division, and identifies a clay that is not as rich in montmorillonite as the Aquagel clay), Zeogel (a trademark of Baroid Division and identifies an attapugite clay used to impart gel strength to salt-water muds), and similar types of clays. The bentonite clays are especially useful with the invention.

Other additives may be incorporated into the microemulsions to impart desired characteristics to the drilling fluids. Such additives are known in the art and include weighting agents such as barium sulfate, lost circulation agents such as plant fibres, shredded rubber, plastic foil, mica flakes, and preservatives, such as chemical bactericides, fungicides, and anti-fermentatives. However, such additives must be compatible with the microemulsion, i.e. they must not react with components of the microemulsion to phase-separate the microemulsion or to impart adverse chemical properties thereto.

To teach preferred embodiments of the invention, Applicants compared their microemulsion drilling fluids to commercially available drilling fluids. Also, Applicants' microemulsions were tested with other components known in the art and the particular preferences necessary for Applicants' microemulsion were substantiated by laboratory experiments. The following discussion presents the laboratory evaluation.

LABORATORY MEASUREMENTS

Laboratory testing of the drilling fluids, is based on standard procedures recommended by the American Petroleum Institute (API Recommended Practice RP 13B, Second Edition, April, 1969). In certain cases, the standard procedures were modified to measure mud properties at elevated temperatures.

MUD WEIGHT

Mud weight or density is expressed in pounds per gallon. In each example, the amount of weighting material necessary to give a weight of ten pounds per gallon was calculated and added to every sample.

VISCOSITY, YIELD POINT AND GEL STRENGTH

These measurements were done with a multi-phase direct-indicating Fann V-G viscometer as recommended by API Recommended Practice 13B, pp 5-6. However, the recommended instrument and procedure were modified to measure the rheological properties of the drilling fluid at elevated temperatures—this was done by wrapping a heating coil around the sample container, and letting the sample and instrument equilibrate to a preselected temperature before measurement.

The viscosity in centipoises is expressed as plastic viscosity and/or as apparent viscosity. Yield point and gel strength are expressed in pounds per 100 sq. ft. The gel strength or thixotropy is measured 10 seconds after the sample has been stirred vigorously and is measured a second time 10 minutes after vigorous stirring—procedure is given in page 6 of API RP 13B.

FILTRATION TESTS

Filtration tests were conducted at room temperature and at elevated temperatures using a high-temperature mud cell defined in U.S. Pat. No. 3,617,868 to Beitel et al.

RESISTIVITY

Resistivity of the drilling fluid is measured at room temperature and at elevated temperature using the mud cell identified in U.S. Pat. No. 3,617,868 to Beitel et al. Resistivity is reported in ohm-meters.

NECESSITY OF USING SODIUM PETROLEUM SULFONATE WITHIN MICROEMULSION

Oil-external microemulsions were made with ammonium petroleum sulfonates. Three common drilling mud clays, i.e. Aquagel, Baroco, and Zeogel (these are trademarks of Baroid Division, National Lead Company, Houston, Texas), were separately added to the microemulsion. All of these three clays caused the microemulsion to phase separate into two to six distinct layers. Some of these layers differed only in amount and particle size of clay but other layers were of different compositions from the original microemulsion. The refractive index measurements of the filtrate from different layers verified phase separation of the microemulsion.

It was rationalized that the reason for phase separation probably was due to the relative order of preference with which cations compete for exchange positions on clay structures. That is, the ammonium cation on the sulfonate is attracted preferentially to the clays where it replaces cations mutually on the clays. Thus, the sulfonate loses the ammonium cation and gains cations which adversely influence the stability of the microemulsion.

An identical microemulsion was made with sodium petroleum sulfonate. Upon addition of the previously mentioned clays, the microemulsion did not phase separate. The composition of the microemulsion is

Component	Amount and Type	
Sodium petroleum sulfonate	8.04	gm Petronate HL.
Hydrocarbon	9.46	gm Pyronate 50
Cosurfactant	37.9	ml Diesel fuel
	1.0	ml p-aryl alcohol/100 ml microemulsion components
Water	29.14	ml water containing 28,000 ppm total dissolved solids.

Petronate HL sulfonate has an average equivalent weight of 450 and an activity of about 62%, and, Pyronate 50 has equivalent weight of about 360, and contains about 50% active sulfonate—these sulfonate trademarks belong to Sonneborn Chemical Co., New York, N.Y., U.S.A. The microemulsion first tested had the same composition except the ammonium petroleum sulfonate replaced the sodium petroleum sulfonate—the ammonium petroleum sulfonate had an average equivalent weight of about 400 and is about 8% active sulfo-

nate These microemulsions are oil-external and phase stable over the temperature range of about 70° to about 185° F

To the microemulsion containing the sodium petroleum sulfonate there is added various amounts of dry Aquagel and Barite (finely divided barium sulfate) The microemulsion did not phase separate However, measured gel strength of the composition was too low for suitable drilling fluids The clay and barite tended to settle from the microemulsion even though the microemulsion was phase stable It is postulated that the clay-water interaction is necessary to impart gel strength, by adding dry clay to the oil-external microemulsion, the clay and water were effectively seques-

lower in the presence of salts, however, with a concentration of 28,000 ppm of TDS in the water, the rheological properties are still within operational range of conventional drilling fluids The rheological properties were determined at 74° F and at different weight concentrations of Aquagel in the microemulsion, the Aquagel was added by first obtaining an aqueous mixture of the Aquagel in water and then adding it to an anhydrous microemulsion stock solution In each case, the mud weight of the microemulsion is adjusted to ten pounds per gallon by adding barite Also, the apparent viscosity is determined at 100 rpm and at a shear rate of 100 rpm = 170.4 sec-11 Rheological properties of particular microemulsions are indicated in Table 1

TABLE 1

Sample*	Weight % Aquagel	Water	Apparent Viscosity (cp)	Gel Strength (10 Sec/10 Min) lbm/100 ft²	Yield Value lbm/100 ft²
A	0.37	distilled H ₂ O	272	4/5	N.M.*
B	0.75	"	320	5/7	"
C	2.24	"	530	11/14	"
D	2.99	"	620	24/33	"
E	2.99	28,000 ppm TDS	130	8.5/6	17

*N.M.=not measurable with available instrument

*The compositions are identical to the microemulsion previously described except the water is replaced by the indicated water within Table 1

tered from one another This adversity was cured by adding the clay in a clay-water suspension rather than adding dry clay to the microemulsion To obtain maximal gel strengths, the clay can be mixed with soft water, or water containing a very minimum salt content and the clay-water slurry added to the microemulsion drilling fluids—e.g. compare Sample D with Sample E in Table 1 However, Sample E which contains 28,000 ppm of TDS still has sufficient gel strength to be operative as a good drilling fluid

It is postulated that the clay, barite and other water dispersible materials are contained within the micelles of the microemulsion and because the microemulsion is thermodynamically stable, the water dispersible materials within the micelles cannot separate due to gravity That is, the micelles contain water and they are thermodynamically dispersed within the oil phase, thus, any water dispersible material within the water is also "thermodynamically dispersed" and will not settle out due to gravity

RHEOLOGICAL PROPERTIES

Rheological properties of the microemulsion drilling fluids are illustrated in Table 1 This particular drilling fluid had a composition identical to that of the previously described sodium petroleum sulfonate microemulsion drilling fluid except where indicated, the water either had 28,000 ppm of TDS (total dissolved solids) or had essentially 0 ppm of TDS As is evident from Table 1, the rheological properties are decidedly

As is evident from the above table, the apparent viscosities and gel strengths increase with increasing clay content. Although the gel strengths are acceptable, the viscosities of the above-indicated microemulsions may be too high for conventional field applications, however, these examples show that oil-external microemulsions obtained with distilled water (distilled water promotes the maximum possible clay swelling) will yield very high viscosities. These high viscosities can be decreased by either increasing the water concentrations or adding salts—see Sample E wherein the water contains 28,000 ppm of TDS and the apparent viscosity is 130 (this corresponds to a plastic viscosity of 83 centipoises) This table also indicates that mud-like gel strength and high viscosity values can be obtained with less than 3% Aquagel—ordinary water-based muds may require 5 to 10% Aquagel to produce similar mud properties. These high viscosity, oil-external microemulsions have particular utility in reservoirs at very high temperatures, e.g. at high temperatures above 200° F where the microemulsion is still stable but the viscosity of the microemulsion is substantially reduced from Table 1 values.

EFFECTS OF TEMPERATURE AND AQUAGEL

Effects of temperature and the concentration of Aquagel in the microemulsion are illustrated in Table 2 The composition of the microemulsion in this Table is identical to that earlier defined except the water is replaced with distilled water

TABLE 2

Sample	Wt.% Aquagel	Temp. F°	Apparent Viscosity (cp at 100rpm)	Plastic Viscosity (cp)	Yield Value lbm/100 ft²	Gel Strength (10 Sec/10 Min) lbm/100 ft²
F	0.75	74	330	N.M.	N.M.	5/7
G	"	100	204	N.M.	N.M.	4/6
H	"	150	93	73	11	5/6.5
I	"	195	58	42	6	5/6
J	2.24	74	590	N.M.	N.M.	11/14
K	"	100	360	N.M.	N.M.	14/19
L	"	140	215	N.M.	N.M.	14/20

TABLE 2-continued

Sample	Wt. % Aquagel	Temp. F°	Apparent Viscosity (cp at 100rpm)	Plastic Viscosity (cp)	Yield Value lbs/100 ft²	Gel Strength (10 Sec/10 Min) lbs/100 ft²
M	"	180	155	78	29	11/23
N	2.99	74	630	N.M.	N.M.	24/33
O	"	100	330	N.M.	N.M.	22 3/33
P	"	140	260	N.M.	N.M.	26/44
Q	"	190	240	85	53	29/67

From Table 2 it is evident that the rheological and thixotropic properties of the microemulsion increase with relatively small increases in Aquagel content. Also, it is evident that the viscosity and yield values decrease markedly with increase in temperature—this is a distinct operational advantage since muds of this type are usually used at relatively high downhole temperatures. The viscosities and yield values above 150° F are comparable to published values for prior art types of drilling muds. Also, the gel strengths increased markedly with increasing temperature—again, this is a distinct advantage.

A commercially available oil-external emulsion drilling mud was obtained from Baroid Division, National Lead Company, Houston, Texas, the drilling mud having the composition

Component	Concentration
Diesel Fuel No. 2	0.537 (bbl)
Water	0.228 (bbl)
Invermul	15 (lb active emulsifier)
Duracore	8 (lb filtrate control)
Petrotone	4 (lb. natural clay)
Geltone	2 (lb synthetic clay)
Barite	349 (lb weight agent)

Properties of the drilling muds are as follows:

Weight, lb/gal	14.5
Plastic viscosity, cp at 74° F	77
Yield Pt., 11/100 sq ft	33
10-Sec Gel, lb/100 sq ft	15
10-min Gel, lb/100 sq ft	18
Elec. Stability, v	520+

The components in the drilling mud are: Invermul (a trademark of Baroid Division, National Lead Co., Houston, Texas, and identifies an active emulsifier readily dispersible in oil), Duracore (a trademark of Baroid Division, identifies a synthetic organophilic colloid), Petrotone (a trademark of Baroid Division, identifies a clay-like material that increases the suspending properties of crude or refined oils and oil muds), and Geltone (a trademark of Baroid Division, identifies a synthetic organophilic colloid). This drilling mud essentially contains diesel fuel and water (applicants' microemulsion also contains these components), but has less of a water/oil ratio than does Applicants' illustrated microemulsion. This oil-external emulsion drilling mud, at 74° F, has a plastic viscosity of 77 cp, a yield point of 33 lbs/100 sq ft., a gel strength of 15 lbs/100 sq ft at 10 sec and 18 lbs/100 sq ft at 10 min. These values are within the range of values for Applicants' microemulsion drilling fluid at elevated temperatures. By comparing this prior art oil-external emulsion drilling mud with Applicants' microemulsion, it is evident that Applicants' microemulsion drilling fluid, at elevated temperatures, has at least equal rheological properties. This is a decided advantage of Applicants' microemulsion drilling fluids over the prior art. Also, if it is desired to lower these rheological properties of

Applicants' microemulsion drilling fluids, the relative concentrations of the components can be adjusted by adding water, salt, etc., to suit the particular needs of a reservoir.

15 FILTRATION AND RESISTIVITY PROPERTIES

The resistivity and filtration characteristics are a function of temperature and Aquagel content, are illustrated in Table 3. In each case the mud weight of the microemulsion is adjusted to 10 lbs per gallon by addition of barite. Also, the composition of the microemulsion is identical to that described previously except the water contains about 600 ppm of TDS or salts.

TABLE 3

Sample	Wt. % Aquagel	Temp. F°	Fluid Loss ml/30 min.	Resistivity ohm-meters
R	0.75	74	4	0.91
S	"	100	4	0.58
T	"	150	4	0.26
U	"	200	8	0.16
V	"	290	13.6	0.04
30 W	2.24	74	<1	0.99
X	"	100	<1	0.73
Y	"	150	2	0.47
Y	"	200	4	0.32
AA	"	280	11	0.30
35 BB	2.99	74	0	1.30
CC	"	100	0	0.89
DD	"	150	2	0.62
EE	"	200	2	0.43
FF	"	290	14	0.36
40 GG	Baroid Water-in-Oil Emulsion Mud	74	0	N.M.+
HH	Emulsion Mud	100	2	"
II	Emulsion Mud	150	2	"
JJ	Emulsion Mud	200	8	"
KK	Emulsion Mud	290	12	"

From Table 3 it is evident that Applicants' oil-external microemulsions have a very low fluid loss or filtration characteristic—this is highly desirable to prevent formation damage or to stabilize the well bore and also has a distinct advantage for log interpretation purposes. The resistivity values of Applicants' oil-external microemulsions are comparable to those of ordinary water-based muds—this is an advantage in electrical logging; most water-in-oil emulsion muds such as are illustrated by Samples GG through KK will not conduct a measurable current and thus are not suited for electrical logging procedures. Applicants' oil-external microemulsions, however, conduct sufficient electrical current to permit electrical logging. Resistivities of Applicants' microemulsions increase with increasing Aquagel content and decrease with increasing temperature.

ADVANTAGES OF OIL-EXTERNAL MICROEMULSION DRILLING FLUIDS

Applicants' oil-external microemulsion drilling fluids enjoy the same advantages as do oil-external emulsion muds over water-based muds, oil-in-water emulsion muds and oil-based muds. However, Applicants' oil-

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external microemulsion muds have advantages over the oil-external emulsion muds in that

- 1 the oil-external microemulsion muds conduct electrical current, this is needed for ordinary electrical logging techniques—most presently used oil-based emulsion muds do not,
- 2 Applicants' oil-external microemulsion drilling fluids use ordinary, untreated bentonite, e.g. the Wyoming bentonite clay, to impart suitable viscosity, gel strength, and filtration characteristics—the currently available oil-external emulsion muds require pretreated clays to make them oleophilic, and also require organic colloids and oil-wetting agents to give the necessary properties,
- 3 Applicants' oil-external microemulsion drilling fluids require less clay than do the presently available oil-external emulsion muds,
- 4 Applicants' oil-external microemulsion drilling fluids are stable over a wide range of salt concentrations—such advantage is an economical advantage as well as an operational advantage—the samples teach oil-external microemulsions containing 28,000 ppm of TDS, this is a salt concentration approaching that of sea water,
- 5 the inherent properties of Applicants' oil-external microemulsion drilling fluids eliminate the need for several classes of drilling fluid additives such as corrosion inhibitors, emulsifiers, filtrate-reducers, lubricants, thinners, and viscosifiers—the properties of the microemulsion can be controlled merely by altering the composition of the principal components, i.e. clay, water, alcohol, hydrocarbon, etc.,
- 6 Applicants' oil-external microemulsion drilling fluids have higher water contents than do the conventional oil-external emulsion muds—this is a decidedly economical advantage, and
- 7 Applicants' oil-external microemulsions are viscoelastic and allow for drag reduction, the emulsions are not viscoelastic. In essence, Applicants' oil-external microemulsion muds are more economical than conventional emulsion muds and conduct sufficient electricity to permit the use of electrical logging techniques.

It is not intended that Applicants' invention be limited by the specifics taught herein. Rather, all equivalents obvious to those skilled in the art are intended to be incorporated within the scope of the invention as defined within the specification and appended claims.

What is claimed is:

1. An oil-external microemulsion drilling fluid which will conduct sufficient electrical current needed for electrical logging of a subterranean formation, the microemulsion comprised of about 15% to about 90% by volume water, about 5 to about 84% by volume liquid hydrocarbon, about 1% to about 30% by volume of a sodium petroleum sulfonate having an average equivalent weight of about 350 to about 525, and about 0.1% to about 15% by weight, based on the water, of a water-dispersible clay, said clay having been incorporated in the microemulsion by mixing it with the water phase and then mixing the clay-water mixture with the remaining ingredients of the microemulsion

2. The microemulsion of claim 1 wherein it contains about 0.01 to about 20% by volume cosurfactant.

3. The composition of claim 2 wherein the cosurfactant is an alcohol containing about 1 to about 20 carbon atoms

4. The composition of claim 1 wherein the liquid hydrocarbon is a refined fraction of crude oil.

5 The composition of claim 1 wherein the petroleum sulfonate is present in concentrations of about 2% to about 20%

6. The composition of claim 1 wherein the petroleum sulfonate is present in concentrations of about 5 to about 10% by volume

7 The composition of claim 1 wherein the average equivalent weight of the petroleum sulfonate is about 400 to about 470

8. The composition of claim 1 wherein the microemulsion contains about 2 to about 6% by weight, based on the water, of the water-dispersible clay

9. The composition of claim 1 wherein the microemulsion contains about 1 to about 10% by weight, based on the water, of a water-dispersible clay

10. The composition of claim 1 wherein the clay is bentonite

11 The composition of claim 1 wherein the clay is comprised of montmorillonite

12. The composition of claim 1 wherein the microemulsion contains barite

13. The composition of claim 1 wherein it contains about 20% to about 75% water

14. An oil-external microemulsion drilling liquid which will conduct sufficient electrical current needed for electrical logging of a subterranean formation, the microemulsion comprised of

1 about 5% to about 78% by volume of liquid hydrocarbon which is crude oil, partially refined fraction(s) of crude oil or refined fraction(s) of crude oil,

2 about 20% to about 75% by volume of water containing about 0.1% to about 15% by weight, based on the water, of a water-dispersible clay,

3 about 2% to about 20% by volume of a sodium petroleum sulfonate having an average equivalent weight of about 350 to about 525,

4 about 0.01% to about 25% by volume of a cosurfactant selected from the group consisting of alcohol, amine, ester, aldehyde, ketone, ether, and mixtures of said cosurfactant, the cosurfactant which is a semi-polar compound containing about 1 to about 20 carbon atoms, and

5 about 0.001% to about 5% by weight of electrolyte which is an inorganic base, inorganic acid, or inorganic salt or combination thereof said clay and said water having been premixed prior to admixture with the remaining components of said microemulsions

15. The microemulsion of claim 14 wherein the cosurfactant contains about 3 to about 16 carbon atoms.

16. The microemulsion of claim 14 wherein the cosurfactant is an alcohol

17. The microemulsion of claim 14 wherein the petroleum sulfonate has an average equivalent weight within the range of about 380 to about 470

18. The microemulsion of claim 14 wherein the cosurfactant has a water solubility of about 0.01% to about 20% at ambient temperature.

19. The microemulsion of claim 14 wherein the hydrocarbon is a refined fraction of crude oil.

20. The microemulsion of claim 14 wherein the water-dispersible clay is present in concentrations of about 2 to about 6%

21. The microemulsion of claim 14 wherein the water-dispersible clay is comprised of bentonite

22. The microemulsion of claim 14 wherein the water-dispersible clay is comprised of montmorillonite

23. The microemulsion of claim 14 wherein the water is soft.

24. The microemulsion of claim 14 wherein the microemulsion contains barite.

* * * * *

[54] **TREATING SUBSURFACE FORMATIONS**

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[22] Filed March 16, 1970

[21] Appl No. 19,574

Related U.S. Application Data

[63] Continuation-in-part of Ser No 726,693, May 6, 1968, abandoned, which is a continuation-in-part of Ser Nos 675,490, Oct. 16, 1967, abandoned, and Ser No. 699,255, Jan 19, 1968, abandoned

[52] U.S. Cl. 175/50, 175/65, 175/66, 252/8 5 P, 166/250

[51] Int. Cl. .. E21b 21/04

[58] Field of Search 252/8 5 M, 8.5 P; 175/40, 50, 175/65, 66, 72, 166/250, 275

[56] **References Cited**

UNITED STATES PATENTS

2,552,775	5/1951	Fischer et al	252/8 5 P
2,689,219	9/1954	Menaul	252/8 5 P
2,702,787	2/1955	Freeland	252/8 5 P
2,953,525	9/1960	Young	252/8 5 P
2,994,660	8/1961	Reddie et al	252/8 5 P

OTHER PUBLICATIONS

Moore, John E., How to Combat Swelling Clays, in Petroleum Engineer, Mar 1960, pp. B- 78, 90, 94, 95,

96, 98- 101

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[57] **ABSTRACT**

Shaley earth formations are drilled or otherwise treated with reduced difficulty through the use of water-in-oil invert emulsion fluids wherein the aqueous phases of the emulsions possess particular water vapor pressures relative to the formations which they contact. The aqueous vapor pressure of an oil-base fluid containing dispersed water is controlled to prevent damage to water-sensitive shale formations by monitoring the vapor pressure of the aqueous phase of the fluid and maintaining a vapor pressure depressant in the aqueous phase in a concentration sufficient to substantially prevent the migration of water from the fluid to the formations. The aqueous vapor pressure of an earth formation is determined. A method and apparatus are disclosed for determining the compatibility of a well fluid with a water-sensitive subsurface formation wherein a substantially unaltered sample of the formation is immersed in the fluid and the direction and extent of water migration between the well fluid and the sample are logged. Improved water-in-oil invert emulsion fluid compositions for drilling and other oil field uses are obtained wherein the aqueous phases of the emulsions possess particular water vapor pressures relative to the formations which they contact.

35 Claims, 8 Drawing Figures

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SHEET 1 OF 5

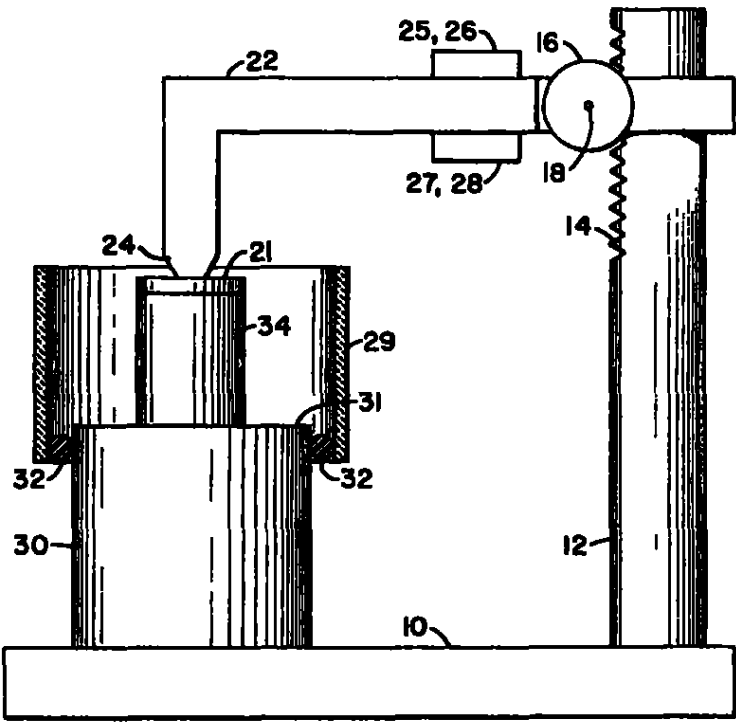


FIG. 1

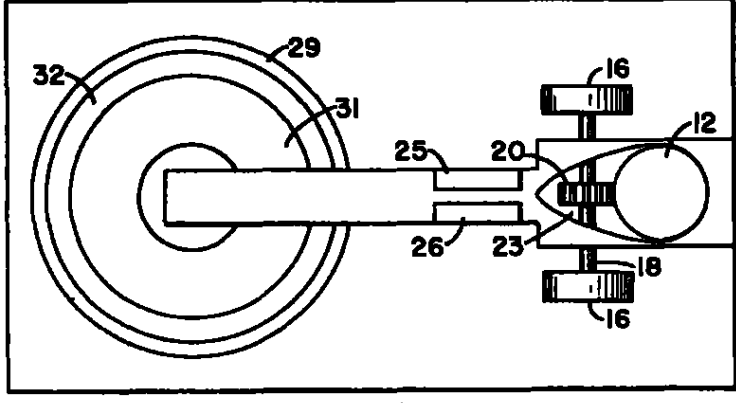


FIG. 2

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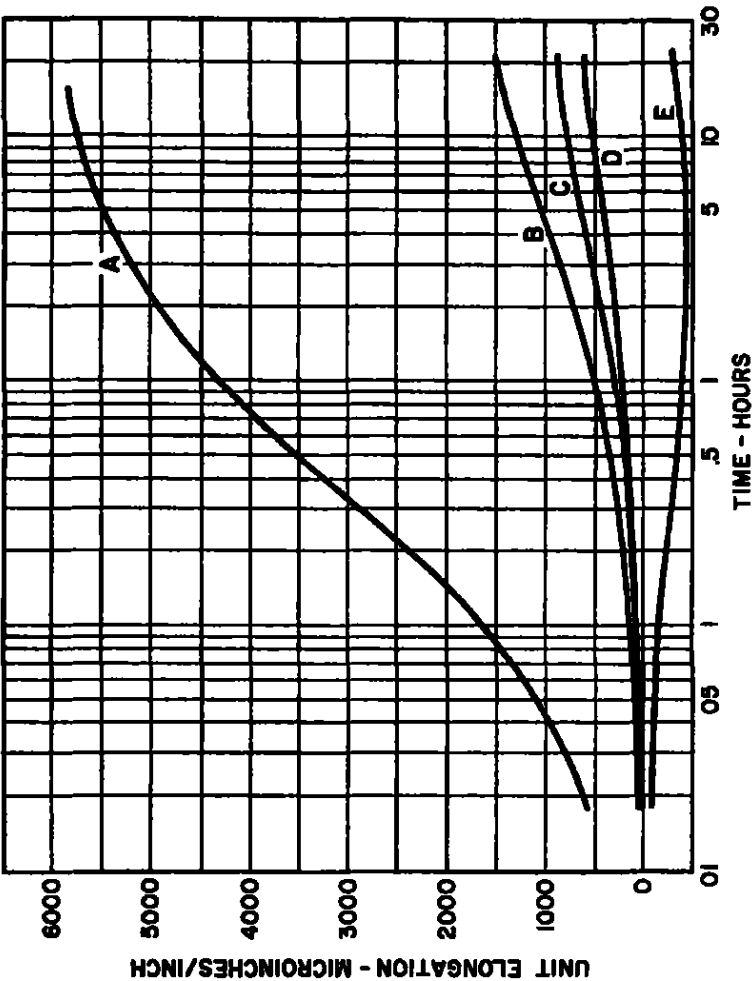
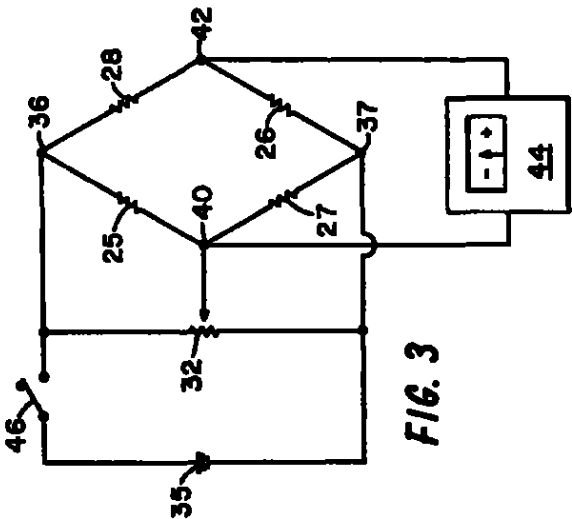


FIG. 4



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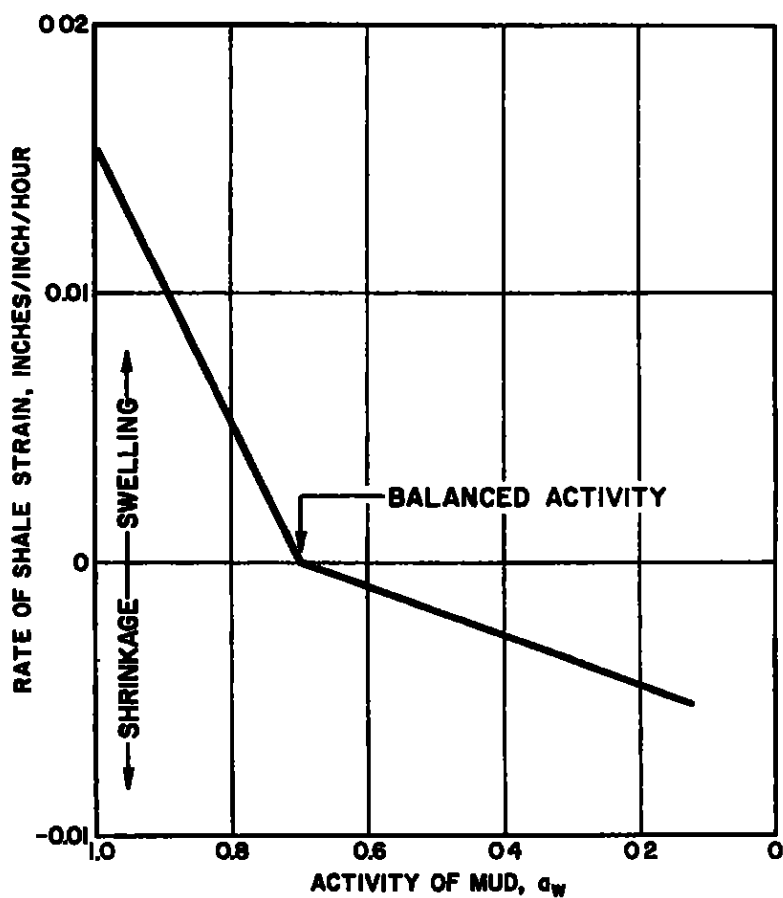


FIG. 5

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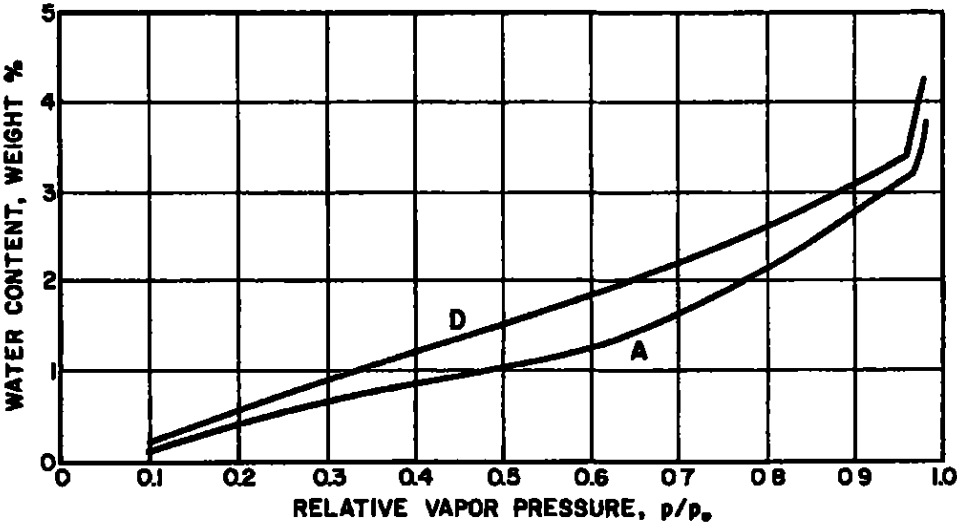


FIG. 6

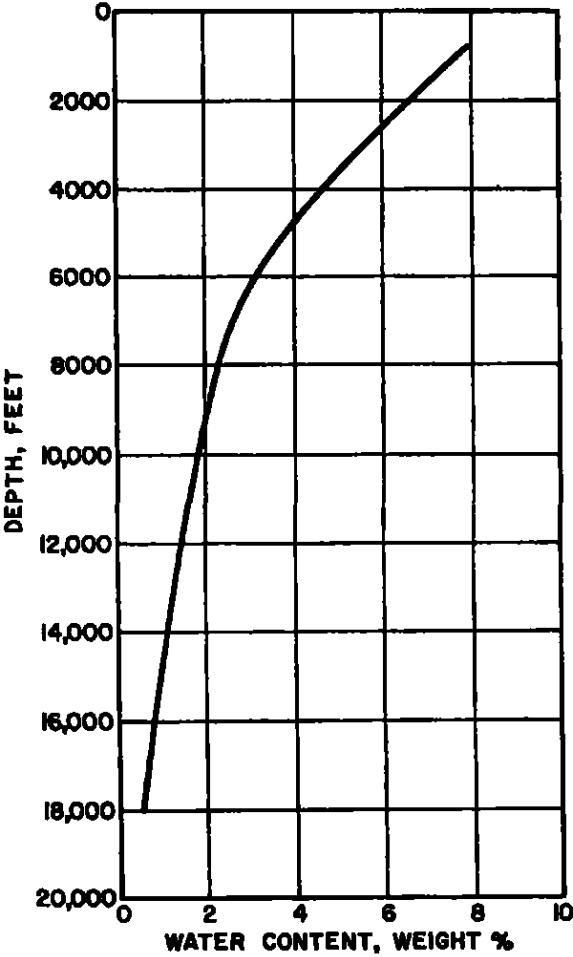


FIG. 7

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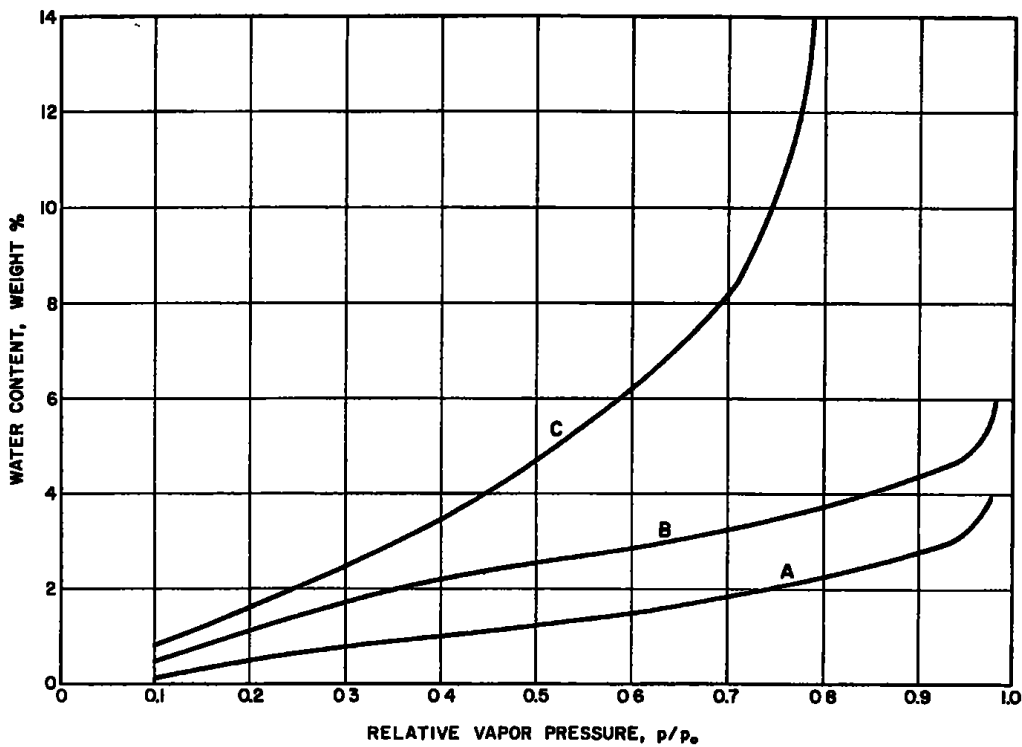


FIG. 8

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TREATING SUBSURFACE FORMATIONS

CROSS REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application, Ser No 726,693, filed May 6, 1968, now abandoned, which was a continuation-in-part of application, Ser No 675,490, filed Oct. 16, 1967, now abandoned, and application, Ser No 699,255, filed Jan 19, 1968, now abandoned

BACKGROUND OF THE INVENTION

1 Field of the Invention

This invention is directed primarily to the drilling of wells through water-sensitive earth formations. More particularly, the invention is concerned with methods for formulating drilling fluids, methods for drilling, and drilling fluid compositions which enable formations to be drilled with a minimum of difficulty. The invention also pertains, in general, to methods for designing and applying fluids which find use in contact with shaley earth formations, and fluid compositions for such use.

2 Description of the Prior Art

The problems encountered in drilling through shales and similar water-sensitive formations are of long standing in the petroleum industry. Such problems are particularly acute in deep formations containing hard shales but are also troublesome in shallower formations. The nature and extent of the difficulties encountered generally depend in part upon the characteristics of the particular water-sensitive formations to be penetrated. Geologically speaking, such formations normally contain fine-grained argillaceous materials which in a compressed state have very low permeabilities, generally less than 0.001 millidarcy. Since such materials may have been deposited under widely different circumstances and subsequently subjected to different temperature and pressure conditions, water-sensitive formations may have mineral compositions and water contents which vary considerably.

Water-sensitive shales are broadly categorized in the petroleum industry as either "soft" shales or "hard" shales. Soft shales are generally considered to include the plastic, gumbo, wet, hydratable, and swelling shales which "dissolve" or disperse readily in water. Soft shales usually occur in young stratigraphic sequences and in the shallower formations within any stratigraphic sequence. "Hard" shales, on the other hand, are hard and are substantially insoluble and nondispersible in aqueous media. They generally contain much less water and montmorillonite than do soft shales. Hard shales generally occur in older, deeper formations.

Soft shales and hard shales both present serious problems during drilling operations. If soft shales are drilled with water or water-base fluids, for example, they may readily disperse or dissolve in the circulating fluid to form a troublesome plastic mass. This dispersion has been generally attributed to the presence of montmorillonite in the shales. Hard shales, on the other hand, do not normally disperse in the fluid but nevertheless quickly lose their strength and break and slough. Until recently there has been no satisfactory or accepted explanation for the failure of hard shales. The extremely low permeabilities of these shales have led observers to theorize that drilling fluids can penetrate

only along the bedding planes and that the failures which occur are due to such penetration. It has also been generally assumed that hard shales are non-swelling in the presence of water.

Difficulties in drilling through gumbo and other soft shales have been alleviated to some extent in the past by the use of water-in-oil invert emulsion muds and other oil-base fluids. The use of invert emulsion muds prepared with saturated sodium chloride solutions or containing moderate amounts of calcium chloride, normally less than 250,000 parts per million, in the water phase of the emulsions has also provided some improvement. The results obtained with such fluids, however, have generally been inconsistent and unpredictable.

Oil-base muds, including water-in-oil invert emulsion muds, have also been used for drilling hard shales. In most instances such use has provided little, if any, improvement over the use of water-base muds. Serious mud losses, formation damage, and increased operating expenses have often been incurred. Although increasing the weight of the drilling fluid and drilling more slowly has often helped, efforts to overcome difficulties encountered with hard shales have in the past been largely unsuccessful.

SUMMARY OF THE INVENTION

This invention provides means for alleviating problems normally encountered when shales and similar water-sensitive argillaceous earth formations are contacted with aqueous fluids. The invention greatly extends the application of oil-base drilling fluids for drilling water-sensitive formations and is especially useful in drilling or treating hard shale formations such as the Midway and Dexter shales in East Texas and West Louisiana, the Wolfcamp shale in West Texas, the Springer and Atoka shales in Oklahoma, and similar hard shales elsewhere.

In accordance with the invention, it has now been found that shales, shaley sands, and similar argillaceous formations, in spite of their extremely low permeability, possess a strong attraction for water and are capable of withdrawing water from water-in-oil emulsions and other fluids with which they come in contact. This sensitivity to water is evidenced by dimensional changes in response to the absorption or desorption of water. These changes, although sometimes very slight, contribute materially to formation failure. It has been found that the rate at which such a formation withdraws water from a particular aqueous fluid is a quantitative measure of the degree of water sensitivity of the formation in the presence of that fluid. This rate and hence the water sensitivity of the formation can be assessed by at least partially immersing a substantially unaltered sample of the formation in the fluid and measuring the changes in dimensions, weight, or other properties of the sample, directly or indirectly, over a selected period. A preferred method of measuring the water sensitivity of the formation is to measure the deformation rate, whether visible or subvisible, of a formation sample in the presence of the fluid.

Although the mechanisms responsible for the transfer of water between the emulsion fluid and the argillaceous shale with which the emulsion fluid comes in contact are evidently complex and are not fully un-

derstood, experience has shown that water transfer from the emulsion fluid to the shale will normally occur if the vapor pressure of the aqueous phase of the fluid is greater than the vapor pressure of the formation. Measurement of vapor pressures thus provides a convenient technique for the evaluation of emulsion fluids. Aqueous vapor pressure is directly proportional to the activity of water and hence water transfer will normally occur from emulsion to shale when the activity of the water contained within the aqueous phase of the emulsion exceeds that of water contained within the shale. It is important to note that the aqueous vapor pressure of the formation normally differs from the vapor pressure of the water or brine contained within the formation. It appears that certain electrical or absorptive forces associated with the matrix or composition of the formation itself greatly decrease the vapor pressure which the water contained therein would otherwise be expected to have. Measurement of the aqueous vapor pressure of the formation, which characterizes the activity of the formation water, is therefore an important aspect of the invention.

Two general methods for designing oil-base drilling fluids in accordance with the invention are disclosed. Both involve the addition of vapor pressure depressants to the aqueous phase of the emulsion fluid in amounts sufficient to eliminate or to retard transfer of water from the drilling fluid to the argillaceous formation. The first method is a direct simulation of the interaction of the fluid and the water-sensitive formation. A water vapor pressure depressant is preferably first dissolved in the aqueous phase of the emulsion drilling fluid. The rate of water transfer between this fluid and the formation is then quantitatively determined by immersing a sample of the formation in substantially its natural state in the fluid and determining the rate of deformation. The concentration of the water vapor depressant can then be increased and additional samples tested until a concentration that reduces the rate of deformation to substantially zero is found. A deformation rate that for all practical purposes approaches zero indicates that the fluid can be used with little likelihood of damaging the formation.

A second method for designing drilling fluids requires that the aqueous vapor pressure of the argillaceous shale formation first be determined. This can be done by exposing formation samples to atmospheres above different saturated salt solutions having known water vapor pressures until equilibrium is reached. By observing the weight change of the sample resulting from water migration, the vapor pressure of an atmosphere that would result in no weight change is determined. This value represents the formation vapor pressure. After thus determining the vapor pressure of the shale formation, an emulsion fluid having an aqueous vapor pressure substantially equal to that of the formation can be prepared. Such a fluid can be used to drill the water-sensitive formation with little likelihood of the hole sloughing.

It is still a further aspect of the invention to provide a method and apparatus to monitor invert emulsion drilling fluids at the well site during drilling operations so that the fluid composition can be changed to compensate for drilling fluid contaminants and the like encountered in the borehole. Another aspect of the in-

vention is to provide improved water-in-oil emulsion drilling fluid compositions. While oil-base fluids and invert emulsion fluids, which are both water-in-oil emulsion fluids, are sometimes distinguished on the basis of water content, all three terms are treated as synonymous herein. It is still another aspect of the invention to provide methods for designing improved coring fluids, treating fluids, fracturing fluids, displacement fluids, and the like which contact water-sensitive formations.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG 1 schematically depicts an elevation view of a displacement transducer instrumented with strain gauges suitable for performing the simulation test method of the invention.

FIG 2 is a schematic plan view of the apparatus of FIG 1.

FIG 3 is a schematic diagram of an electrical circuit that can be used with the apparatus of FIG 1.

FIG 4 graphically illustrates unit elongation versus log time data recorded while testing a hard shale in accordance with the simulation test method of the invention.

FIG 5 graphically illustrates the rate of deformation exhibited by a number of samples of an argillaceous shale formation contacted by water-in-oil emulsion drilling fluids having different aqueous activities.

FIG 6 shows the water vapor pressure (P), relative to the vapor pressure of pure water (P_0), exhibited by a West Texas hard shale at 25° C for various water contents within the shale.

FIG 7 is a correlation showing the average variation in the water content of a shale in terms of depth of burial within the earth.

FIG 8 is a correlation showing the average vapor pressure (P) of two hard shales and one soft shale relative to the vapor pressure of pure water (P_0) at 25° C for different shale water contents.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

I Design of Drilling Fluids

A The Simulation Test Method

1 Nature of the Simulation Test Method

The simulation test is based on the discovery that the rate at which shales and other argillaceous formations absorb water from a particular aqueous fluid is a quantitative measure of the degree of water sensitivity of the formation in the presence of the fluid. The test is performed by at least partially immersing a sample of the formation which is in substantially its natural state of hydration in the drilling fluid of interest and determining the rate of water absorption.

One method for determining the water absorbed is by change of weight of the sample. The sample is weighed initially and its change in weight observed over a period of time. Any change in weight which occurs is attributable to the migration of water. Weight measurements can be obtained while the sample is immersed by suspending it in the drilling fluid and periodically recording the suspended weight. In lieu of this, the sample may be withdrawn from the fluid after a fixed period of time, cleaned, and then weighed. Another method recognizes that the resistivity of the sample will

decrease as it absorbs water and utilizes changes in resistivity to measure the amount of water absorbed. Still other methods are based on the measurement of changes in sonic velocity, compressive strength, and other physical properties which vary with water content to indicate the rate of absorption.

The preferred method of measuring absorption is to log the rate of change in dimensions of a shale sample while it is immersed in the drilling fluid. This gives a direct measurement of the deformation of the shale due to the drilling fluid and thus provides a quantitative measurement of the rate of water absorption. A wide variety of devices for recording changes in dimensions may be used, including micrometers, optical equipment, dial displacement indicators, and the like. The preferred apparatus, however, is a displacement transducer instrumented with strain gauges.

2 The Displacement Transducer Apparatus

FIGS 1 and 2 illustrate a resistance strain gauge displacement transducer suitable for measuring the change in dimensions of a sample of shale or similar material. This apparatus includes a rectangular base 10 from which a substantially cylindrical column 12 extends vertically. A series of beveled teeth on the upper portion of column 12 form rack 14.

Cantilever deflection beam 22 engages rack 14. The outermost end of the deflection beam extends downwardly in an L-shape terminating in a frusto-conical end terminus 24. Contactor shoe 21 is mounted on end terminus 24. The innermost end of the deflection beam 22 contains a generally oval aperture 23, one end of which forms a yoke that fits over upright column 12 and forms a slidable support with the column. Shaft 18 passes through deflection beam 22 at the other end of aperture 23. Knobs 16 are mounted on the ends of shaft 18. Pinion 20 is supported on the shaft 18 in a position corresponding to the middle of the aperture to cooperate with rack 14. Upper strain gauges 25 and 26 are mounted on the upper side of deflection beam 22. Lower strain gauges 27 and 28 are positioned on the other side of the beam.

A cylindrical pedestal 30 extends from a rectangular base 10 underneath contactor shoe 21. The upper surface 31 of the cylindrical pedestal is smooth and forms a bearing surface underneath shale sample 34. Cylindrical cup 29 slides upon cylindrical pedestal 30. Sealing member 32 is mounted between the cup and the pedestal to prevent the leakage of fluids.

FIG 3 illustrates an electrical circuit suitable for use with the strain gauge displacement transducer apparatus. A four-resistor electrical bridge in which strain gauges 25, 26, 27, and 28 form the resistors is shown. At least four resistors are generally used to obtain increased amplitude and inherent temperature compensation. Variable resistor 32 is placed in the circuit to balance the bridge prior to strain measurements. Voltage source 35 creates a difference in potential across resistor 32 and across the bridge between contacts 36 and 37, causing direct current to flow through resistor 32 and the legs of the bridge formed by resistors 25 and 27, and 26 and 28, respectively. Voltage is measured between terminals 40 and 42 by voltmeter 44. In lieu of this, a suitable strain indicator, such as Model P-350 sold by The Budd Company, Phoenixville, Pennsylvania, could be used. Switch 46 is used to turn the

strain gauge transducer on and off. Although the relatively simple strain gauge circuit illustrated is suitable, other circuits such as those illustrated in M. Hetenyi's book, *Handbook of Experimental Stress Analysis*, John Wiley & Sons, Inc., New York, New York (1950) could readily be adopted.

Prior to using the strain gauge transducer, it must be calibrated to determine the relationship between observed voltages and displacement. This can be done by first zeroing the voltmeter, as is discussed below, and then placing successively larger or smaller articles of known length between contactor shoe 21 and cylindrical pedestal 30 and observing the voltages. From these data a constant that relates voltage and displacement can be obtained.

To use this equipment to analyze the compatibility of a drilling fluid and a particular shale, a sample of the shale should be placed on surface 31 of cylindrical pedestal 30. Deflection beam 22 is then lowered by turning knob 16. This rotates shaft 18 on which pinion 20 is mounted. Pinion 20 cooperates with rack 14 to convert the rotational movement of the knob 16 into a downward translational movement of beam 22. The beam should be lowered until contactor shoe 21 engages the shale sample 34 and holds it firmly in place on surface 31 of the pedestal 30.

With the shale sample thus mounted, the strain gauge's electrical circuit should be balanced. Voltage source 35 is energized by closing switch 46, causing current to flow through variable resistor 32 and both sides of the resistance bridge. The bridge is balanced by adjusting variable resistor 32 until voltmeter 44 is zeroed. Once the bridge has been balanced, the voltage readings will indicate deformation. Cylindrical cup 29 is then raised to its uppermost position so that the upper edges of the cup are above the top of sample 34. Sufficient drilling fluid to cover the sample is then poured into the cup held between contactor shoe 21 and surface 31 of cylindrical pedestal 30.

Once the drilling fluid contacts the sample mounted within the strain gauges, the sample will begin to absorb water and expand if it is incompatible with the fluid. Expansion of the sample will force contactor shoe 21 upward, deflecting beam 22. Deflection of the beam results in deformation of the strain gauges and produces an imbalance in voltage readings across the bridge. If the fluid absorbs water from the sample, the sample will generally exhibit shrinkage. Such shrinkage also normally produces an imbalance in voltage readings across the bridge. However, these voltages will have an opposite sign from those caused by swelling.

Several voltage readings should be taken at various times after the sample has been immersed in the drilling fluid. The voltage readings are proportional to the displacement of the sample between contactor shoe 21 and pedestal 30. The relationship between displacement and time can be determined from the calibration constant and used to determine the rate at which the sample will absorb water from the particular drilling fluid. When comparing data, it is useful to normalize the displacement data by dividing each reading by the sample length. The normalized data is then referred to as "strain." The rate so determined is indicative of the degree of compatibility between the water-sensitive formation and the drilling fluid.

3 Selection and Preparation of Formation Samples

The determination of the water sensitivity of a sub-surface formation in the presence of a particular drilling fluid in accordance with the invention is normally carried out with a sample of the formation having substantially its in situ composition. Exposure to high temperatures and other treatment that may alter the composition should be avoided. It is preferred that this sample be in substantially its natural state of hydration so that its surface absorption behavior will approximate in situ absorption behavior. Laboratory tests performed at reservoir conditions of temperature and pressure, when compared with absorption tests conducted under atmospheric conditions, indicate that atmospheric tests are sufficiently accurate for most practical purposes.

The formation samples utilized may be preserved core samples from the subject well or from a nearby well that penetrates the same formation. Such preserved samples are particularly representative when the coring fluid used inhibits absorption of water by the water-sensitive formation. Fragments of the formation entrained by the drilling fluid and carried to the surface can also be used. Since a water-sensitive formation will begin hydration as soon as it is contacted with a water-containing drilling fluid, it is preferable that such fragments be recovered as early as possible after initial contact of the rock by the fluid. Hence, the depth of the formation of interest should be estimated and samples from the earliest returns from drilling the formation should be secured for the test. The use of an oil-base drilling fluid treated in accordance with the invention generally simplifies the recovery of samples in substantially their natural state of hydration.

Where severe hydration of the formation has occurred, the samples obtained should be restored to their natural state of hydration. Hydration is not always encountered when the drilling fluid is a treated oil-base fluid and is generally more severe where a water-base fluid is used to drill a highly water-sensitive shale. Restoration to a substantially natural state can be accomplished by baking the samples at a temperature slightly above 100° C until sample density corresponds with typical shale density for this formation and depth of burial. Sample density can be rapidly determined by means of a graduated density liquid column, the mercury pump pressure chamber method, or other suitable techniques. Correlations of shale density versus depth of burial are available in the literature for various formations and are typified by those published by K. F. Dallmuis in his study "Mechanics of Basin Evolution and Its Relation to the Habitat of Oil in the Basin," *Habitat of Oil - A Symposium*, Tulsa, Amer. Assoc. Petrol. Geol., 1958, p. 883-931. It is important that temperature not greatly exceed 100° C since excessive temperatures may result in substantial changes in characteristics of the sample.

4. Drilling Fluid Design

Use of the method and apparatus of the invention to formulate an oil-base drilling fluid that will prevent or minimize absorption and thus promote borehole stability is based in part on the observation that an oil-base or water-in-oil emulsion mud having an aqueous vapor pressure substantially equal to or less than that of the troublesome water-sensitive formation will prevent absorption of water by the formation. Samples of the water-sensitive formation in substantially their natural state should be used, as indicated above. Several of

these samples are preferably immersed in a corresponding number of different oil-base drilling fluids having different aqueous vapor pressures and strain-time data are obtained for each fluid-formation combination. This procedure can be greatly expedited by using a number of strain gauge displacement transducers.

A series of water-in-oil emulsions or other oil-base muds having different aqueous vapor pressures can be prepared by adding various concentrations of inorganic salts such as NaCl or CaCl₂ to the mud. A number of other vapor pressure depressants are discussed herein in connection with the method of determining the vapor pressure of an earth formation. Suitable vapor pressure depressants are not limited to these or similar inorganic salts, however. Any solute introduced into the aqueous phase will reduce the aqueous vapor pressure.

FIG. 4 illustrates strain-time data obtained in accordance with the invention for the hard, argillaceous Wolfcamp shale. Fluid A is water, and the high rate of absorption for this fluid is typical of a very compatible fluid. Fluids B, C, D, and E are water-in-oil invert emulsions containing in the aqueous phase, as vapor pressure depressants, 130,000-ppm NaCl, 200,000-ppm NaCl, 270,000-ppm NaCl, and 450,000-ppm CaCl₂, respectively. Curves B, C, and D illustrate the reduction in absorption that occurs as the concentration of the aqueous vapor pressure depressant is increased and the aqueous vapor pressure of the fluid approaches that of the formation. Curve E illustrates behavior characteristic of a water-in-oil emulsion mud with an aqueous vapor pressure that has been reduced below that of the water-sensitive formation. Instead of swelling, the shale sample shrinks, indicating that water is being desorbed from the shale sample. The use of a drilling fluid with a composition similar to that of mud E would therefore prevent absorption of water by the shale. Generally, however, there is little incentive in attempting to dehydrate a water-sensitive formation and therefore such a fluid would normally be considered to contain an excessive amount of vapor pressure depressant. In most cases it would be more economical to reduce the concentration of CaCl₂ in Fluid E so that its strain-log-time curve would more closely approach the zero strain line than to use a mud such as Fluid E.

FIG. 5 illustrates graphically the rates of deformation of a series of shale samples exposed to invert muds having varying aqueous activities (relative vapor pressures). The shale formation on which the tests were run had an aqueous activity of 0.7. Each test involved immersing a shale sample in an invert mud having a known aqueous activity for a period of 10 hours, measuring the strain, and then computing the average rate of strain of the sample over this time period. It will be noted that shale samples exposed to muds having aqueous activities higher than 0.7 swelled and that the observed rate of swelling increased as the difference in aqueous activity between the mud and the sample increased. Samples contacted with muds having aqueous activities lower than 0.7 shrank. Again, however, the rate of deformation increased in relation to the activity difference. These data demonstrate that when a difference in activity exists, water will flow either from the emulsion mud to the shale or from the shale to the mud.

The former causes swelling of the water-sensitive subterranean formation, leading to its sloughing into the wellbore, the latter increases the water content and thus viscosity of the drilling fluid, necessitating frequent additions of oil, salt and other materials required to maintain the drilling fluid. However, when the activity of the mud is substantially equal to that of the shale formation being drilled, a unique relationship exists. So long as this balanced condition is maintained, there is substantially no migration of water in either direction. Thus, it is especially desirable to maintain the aqueous activity of the mud about equal to that of the shale and thereby both eliminate sloughing of the borehole and obviate the addition of salt, oil or other materials to the mud normally required when it is contaminated by water.

Although the simulation test has been discussed in relation to water-in-oil emulsion drilling fluids the utility of the simulation test is not limited to this type of drilling fluid. The simulation test method and apparatus can be used to determine the compatibility of any drilling fluid with a water-sensitive formation and can be employed to select the most compatible drilling fluid from any group of drilling fluids. The method and apparatus can also be used to determine whether or not a particular formation is water-sensitive and to select fluids for use in secondary recovery, well stimulation, or other well operations, as is more fully discussed subsequently herein.

B The Formation Vapor Pressure Test Method

1 The Method of Determining the Vapor Pressure of an Earth Formation

The aqueous vapor pressure of a shale or other water-containing earth formation can be determined by subjecting a sample of the formation to air of a constant known humidity for a period of time sufficient for moisture within the shale to reach equilibrium with the moisture in the air. It will normally be difficult to preselect a humidity condition such that the natural water content of the shale will be in equilibrium with this condition of humidity. So, generally speaking, several different humidity conditions must be used to obtain a range of water contents within the sample which will span the in situ water content of the formation within the earth.

A very convenient procedure for exposing samples of a given formation to air of different humidities is to suspend or place the sample in a sealed container in an atmosphere of air above a saturated aqueous solution of a solute which contains an excess of undissolved solute. Thus, it is known that the relative humidity of the enclosed space above such a solution where the sample has been placed will remain substantially constant at a given temperature—conveniently room temperature (25° C). An article containing an explanation of this principle and also listing a number of saturated solutions and solutes is contained in *Ecology*, Vol. 41, No. 1, pp 232-237 (January, 1960). Typically, a series of several different saturated solutions can be prepared, and one or more samples of a given shale or other formation can be exposed to an enclosed atmosphere above each of these samples for a sufficient period of time for equilibrium to occur. Complete equilibrium will normally take about 1 or 2 weeks, but substantial equilibrium can normally be attained in about 1 or 2 days.

As noted above, a number of different saturated aqueous solutions should be selected such that a given formation sample is equilibrated at a range of relative humidities. The use of 8 to 10 different relative humidities ranging from about 10 percent relative humidity to 95 percent or more relative humidity has been found to be very desirable and effective. In this connection, it has been found to be quite effective to use the following saturated solutions to obtain a suitable range of atmospheres. The solutions and the relative humidities which exist above these solutions are listed below.

Saturated solution of	Relative humidity (%)	at 25°C
15 ZnCl ₂ 1½ H ₂ O	10.0	
CuCl ₂ 6H ₂ O	29.5	
Ca(NO ₃) ₂ 4H ₂ O	50.5	
NH ₄ Cl + KNO ₃	71.2	
(NH ₄) ₂ SO ₄	80.0	
Na Tartrate	92.0	
20 KH ₂ PO ₄	96.0	
K ₂ Cr ₂ O ₇	98.0	

Many of these salts, incidentally, may themselves be used within the aqueous phase of invert emulsions for the purpose of establishing the vapor pressure of that phase. If vapor pressures less than that obtainable for a saturated calcium chloride solution are desired, solutions of ZnCl₂ 1½ H₂O, LiCl H₂O, ZnBr₂ LiBr 2H₂O; potassium hydroxide or other stronger vapor pressure depressant may be employed. The depressant, of course, must be compatible with the invert emulsion of interest, and such compatibility should be tested prior to actual use.

After a formation sample has reached equilibrium with a particular atmosphere of known relative humidity, the sample should be withdrawn from the atmosphere and its water content promptly determined. A simple procedure for determining its water content is to weigh the equilibrated sample, and then repeat the weighing after the sample has been dried at about 105° C for a period of 12 to 24 hours. The loss in weight of the sample is a direct measure of the equilibrated water content of the sample. The vapor pressure of the sample for this water content is the vapor pressure of water at room temperature (or the temperature of the equilibrium condition) multiplied by the percent relative humidity of the air in equilibrium with the sample.

After the vapor pressures and water contents of a given sample or set of samples have been determined, these values can be recorded on a suitable chart or other record medium and intermediate values can be determined from the resulting correlation. Thus, FIG 6 of the drawing shows two correlations (A for absorption conditions, and D for desorption conditions) obtained by subjecting samples of a West Texas hard shale to eight different conditions of relative humidity ranging from 10 percent relative humidity to 98 percent relative humidity at a temperature of 25° C. These curves also apply for temperatures at least as high as 100° C. As can be seen, slightly different correlations were obtained for tests in which water was desorbed from the shale samples as compared with tests in which water was absorbed by the shale samples. The shale sample in this instance had an in situ water content of 2.22 weight percent as determined by analyzing a small central portion of a core cut directly from the forma-

tion under conditions such that the water content of most of the core was undisturbed. From FIG 6, it is apparent that this formation has a water vapor pressure (or "formation vapor pressure") relative to the vapor pressure of pure water of between about 0.71 and 0.81.

Another convenient method for determining the aqueous vapor pressure of a water-sensitive formation is to place a sample that is representative of the subsurface formation in a sealed container until it reaches equilibrium with the enclosed atmosphere. A direct measurement of the relative humidity of the formation sample can then be made. This method is also useful for determining the aqueous vapor pressure of a water-containing oil-base drilling fluid. Apparatus for measuring relative humidity is widely available. Typical of such apparatus is the Catalog No. 2200 ELECTRO-HYGROMETER that is sold by Lab-Line Instrument, Inc., Melrose Park, Ill.

2. Selection and Preparation of Samples

As indicated earlier, the use of this invention in designing well fluids should be preceded by a determination of the vapor pressure characteristics of the portions of the zones or formations which the emulsion fluid will contact. In the case of a drilling operation, as pointed out earlier in the discussion of the simulation test, a sample of the formation of interest should be obtained so that its vapor pressure can be determined. If a sample of the formation is not obtainable directly from the well being drilled, then an effort should be made to obtain a sample from a nearby well. It is also possible, however, to collect and use cuttings from the well which is being drilled.

Again, the preferred type of formation sample to obtain and study is a sample from the central portion of a core which has been cut from the formation under conditions suitable to preserve the natural conditions of the core as much as possible. If such a sample is available, a reasonably accurate determination can be made of the amount of in situ water contained in the core. If such a core cannot be obtained, the formation's water content can be estimated from FIG 7. FIG 7 is a correlation showing how the water content of many shaley formations within the earth vary, on the average, with increasing depth of burial. Thus, if a given formation lies about 10,000 feet beneath the surface, it may be expected to have, on the average, a water content of about 2 weight percent. It is then possible to use this water content, in combination with the method described earlier for determining the vapor pressure of a formation within the earth, to arrive at an approximate value of the vapor pressure possessed by the formation in its natural condition within the earth.

3. Drilling Fluid Design

Once the formation vapor pressure is known, it is then possible to select and formulate a water-in-oil drilling fluid having an aqueous phase vapor pressure which bears a particular relation to the aqueous vapor pressure of the formation. Generally speaking, it is desirable that the aqueous phase of the drilling fluid have an aqueous vapor pressure no greater than that of the water-sensitive formation. This frequently requires the aqueous vapor pressure of the drilling fluid to be less than that of a saturated sodium chloride solution and often it is desirable to saturate the aqueous phase of the drilling fluid with calcium chloride. As pointed

out above with respect to drilling fluid design by the simulation method, it is especially desirable to maintain the aqueous activity of the mud at a level about equal to that of the water-sensitive formation. Balancing the activities in this fashion eliminates any substantial migration of water between the emulsion fluid and the formation, thereby eliminating any sloughing of the borehole as well as contamination of the mud by water contained within the shale.

However, economics or other considerations may occasionally make it undesirable to attempt to completely reduce the aqueous vapor pressure of the drilling fluid to that of the formation. As long as the water transfer between the fluid and formation is insufficient to cause excessive formation failure during the time period the water-sensitive formation is exposed to the wellbore, the aqueous vapor pressure of the drilling fluid can be considered to be substantially equal to that of the water-sensitive formation. However, it is preferable to reduce drilling fluid vapor pressure to a level that is equal to or below that of the formation.

It should be noted that mixtures of salts can be used in the water phase of an invert, but such mixtures are subject to the common-ion effect. Their aqueous solutions may thus have higher aqueous vapor pressures than would otherwise be suggested by the total salt concentration. It should also be noted that the emulsifier and other water-soluble constituents of the drilling fluid may tend to slightly alter the vapor pressure of the aqueous solution containing the vapor pressure depressants when the emulsion fluid is prepared. Thus the aqueous vapor pressure of the emulsion fluid, which is the aqueous vapor pressure of the water phase of the emulsion fluid, may differ slightly from that of the aqueous salt solution used to prepare the emulsion. Generally speaking, however, an invert emulsion drilling fluid wherein the aqueous phase is saturated with sodium chloride may be used where the vapor pressure of the formation has a value (P_f) about three-fourths of the vapor pressure of water (P_w) at the same temperature (i.e., a relative vapor pressure of 0.75). Referring to FIG 8, such a mud would be successful in drilling the deep, hard, West Texas shale (A) shown there which possesses a natural water content of about 2.2 weight percent. In that regard, it should be noted that hard argillaceous shales seldom exhibit relative aqueous vapor pressures in excess of 0.75. The deep, hard, Louisiana shale (B), for example, would normally be drilled with an invert emulsion fluid wherein the aqueous phase consists of saturated calcium chloride solution (i.e., a relative vapor pressure of 0.30). This shale has a connate or natural water content of about 1.8 or 1.9 weight percent. The soft, gumbo shale (C) has a connate or natural water content of about 11 weight percent and is best satisfied by a fluid with an aqueous phase vapor pressure less than a saturated aqueous NaCl solution.

C. Emulsion Drilling Fluids Designed by the Methods of the Invention

Referring specifically to water-in-oil invert emulsion drilling fluids, a variety of such fluids are commercially available for use in drilling wells. Fluids of this type may be modified by the addition of vapor pressure depressants and can be used for drilling through water-sensitive formations difficult to drill with the commer-

cial fluids. Typical invert emulsion drilling fluids contain droplets of water finely dispersed or emulsified in an oil base. Diesel fuels, kerosenes, and high-gravity crude oils are frequently used as the oil base, and about 10 to 70 percent of fresh or common salt water is emulsified therein with the help of suitable emulsifying and stabilizing agents. Anionic, nonionic, and mixed anionic-nonionic emulsifiers are all used for this purpose. The emulsifiers and stabilizing agents employed in the fluids should be compatible with sodium chloride, calcium chloride, or whatever water vapor pressure depressant is to be incorporated in the aqueous phase of the modified compositions. One specific invert emulsion drilling fluid composition which has been tested and appears satisfactory for many applications comprises 70 volume percent No. 2 diesel fuel, 25 volume percent water saturated with calcium chloride, and 5 volume percent sorbitan mono-oleate as the emulsifier. No difficulty, however, has been encountered in obtaining other satisfactory compositions simply by adding sodium chloride or calcium chloride to certain existing commercially available invert emulsion drilling fluids. Where formations are particularly water-sensitive it may be desirable to prepare a drilling fluid having a vapor pressure which is less than that of a mud containing a saturated calcium chloride solution. Solutions containing ZnBr_2 , ZnCl_2 , LiBr , LiCl , or similar water-soluble salts can be employed for this purpose. In addition, it has been found that a supersaturated CaCl_2 mud can be formed by adding additional CaCl_2 to a mud having a saturated CaCl_2 solution as the aqueous phase. Such supersaturated CaCl_2 muds have vapor pressures lower than those of saturated CaCl_2 muds. Other water vapor depressants contemplated to be useful in the various embodiments of this invention include still other water-soluble salts, phosphoric acid, acetic acid, and other water-soluble acids, glycerol, sodium hydroxide, potassium hydroxide, etc.

D. Monitoring the Drilling Fluid at the Wellbore

Once a compatible drilling fluid has been selected and introduced into the drilling system, it is advisable to monitor the fluid periodically to insure retention of compatibility. Contaminants, absorption, and other phenomena may cause gradual changes in the composition of the mud. Monitoring can be rapidly accomplished by periodically immersing samples of successive formations penetrated by the well in portions of the mud in contact with these formations and logging the direction and extent of water migration between each such sample and the mud in which it is immersed with the displacement transducer apparatus.

In some cases it may be desirable to monitor the mud with calibrated shale samples having known vapor pressures. These calibrated samples may be preserved samples of the formation being drilled that have been taken from another well. Synthetic shale specimens, clay specimens, and the like, prepared so that they have particular aqueous vapor pressures can also be used. Calibrated shale samples representative of the water-sensitive formation are equivalent to substantially unaltered formation samples and the necessity for obtaining such samples from the well being drilled can thus be eliminated. By comparing an oil-base fluid of unknown aqueous vapor pressure with shale samples having known aqueous vapor pressures, it is apparent that the

vapor pressure of the fluid can be determined. In this connection, it may be desirable to continuously monitor the aqueous vapor pressure of the oil-base mud with the displacement transducer and compare it with the formation vapor pressure. Another convenient method to monitor the aqueous vapor pressure of the mud is to place a sample in a closed container and directly measure the relative humidity of the atmosphere in contact with the samples as is discussed above.

The condition and composition of the oil-base fluid can be determined by periodically emulsion-breaking a mud sample and determining its water content. In addition, the water can be analyzed for its content of vapor pressure depressant. Thus, if the vapor pressure of the aqueous phase is being controlled by the presence of calcium chloride, the aqueous phase can be analyzed for this salt.

The condition of the drilling fluid can also be qualitatively evaluated by observing the cuttings produced in the drilling operation if the water-sensitive formation is such that it will undergo visible deformation as it absorbs water. If the cuttings are firm and uniform, it can therefore be inferred that the fluid and the formation are in satisfactory condition. On the other hand, if the cuttings become softer or more diffuse, the concentration of the vapor pressure depressant in the aqueous phase of the fluid should be increased.

If an invert emulsion drilling fluid prepared in accordance with the invention loses water from its aqueous phase during drilling, it is probable that the water is being absorbed by the surrounding formation, and if this is the case, drilling conditions will tend to become more adverse. It is therefore desirable, under such circumstances, to add vapor pressure depressant to the aqueous phase of the fluid until its aqueous vapor pressure is no greater than the aqueous vapor pressure of the formation being drilled. This can generally be done by vigorously mixing the fluid at the surface of the earth with fresh depressant.

As noted previously, drilling fluids prepared in accordance with the present invention are especially applicable for use in the drilling of hard shales. Until the advent of this invention, there has been no satisfactory procedure for dealing with such shales. As noted previously, such hard shales generally have aqueous activities less than 0.75 which corresponds to a saturated solution of NaCl . The results obtained in accordance with the invention have shown that invert emulsion muds wherein the aqueous phase is water saturated with calcium chloride are remarkably effective for a wide variety of such shales. If, during the course of drilling such a shale, additional calcium chloride must be added to the mud system, this may be done by mixing powdered calcium chloride into the fluid. Powdered calcium chloride has been found to readily enter the aqueous phase of an invert emulsion drilling fluid.

Abnormal pressure zones represent serious drilling hazards in many areas where wells are drilled. One characteristic of such zones is a transition zone that lies just above the abnormal pressure zone and that exhibits a marked increase in water content. Since a corresponding increase may also be observed in the water activity of shales in the transition zone, continuously logging the activity of formations penetrated provides a method of detecting abnormal pressure zones. Water

activity of a shale is reflected by the ratio of its aqueous vapor pressure to the vapor pressure of pure water at the same temperature, i.e., relative humidity. It may therefore be desirable to log the aqueous vapor pressure of the drilling cuttings of the formations as they are penetrated. Measurements can be performed by exposing the cuttings to atmospheres of varying known humidities as discussed above, by placing the cuttings in a closed container and directly measuring the relative humidity of the atmosphere in contact with them as also discussed above, or by using the displacement transducer apparatus in conjunction with a series of oil-base fluids having known aqueous vapor pressures. If the aqueous vapor pressure of the shale is equal to that of the oil-base fluid, when the shale sample is placed in contact with the fluid it will exhibit no deformation.

II Used of the Methods of the Invention for Other Fluids

A Treating Fluids

The principles of this invention are also applicable to otherwise conventional well fluid compositions such as packer fluids, coring fluids, completion fluids, and well treating fluids. With respect to treating fluids, for example, the methods and apparatus of the invention are useful in designing fluids for repairing and restoring water-damaged formations. In the past, it has been conventional practice in the field to attempt to restore water-damaged formations by treating them with concentrated salt water (30,000-50,000 ppm) or with solvents such as alcohols which have at least some degree of miscibility with both water and hydrocarbons. In accordance with the present invention, a suitable treating fluid is a water-in-oil emulsion wherein the aqueous phase has a sufficiently low vapor pressure so as to attract water from the damaged formation, thereby dehydrating and restoring the formation. Suitable oils for use in the emulsion include diesel fuels, kerosenes, light fuel oils, light crude oils, light petroleum fractions, LPG's, and the like. Oil-base and water-in-oil invert emulsion drilling fluids containing vapor pressure depressants are also generally suitable for use as packer fluids, coring fluids, completion fluids, etc.

B Displacement Fluids

The principles of the invention are also applicable to fluid compositions and methods used in displacing oil from reservoirs. In recent years, for example, it has been observed that water-in-oil emulsions and microemulsions are useful in displacing oil from reservoirs. Such fluids generally are prepared from the same types of oils used to prepare invert emulsion treating fluids. Soluble oils have been employed to form microemulsion displacement fluids. Such formulations are typified by the displacement fluids disclosed in U.S. Pat. No. 3,254,714. The emulsion or microemulsion is injected into a reservoir at one point and driven from that point through the reservoir toward a second point where displaced oil is recovered from the reservoir. Since such emulsions and microemulsions have a substantial degree of miscibility with reservoir oils, and since their viscosities can be controlled to a considerable degree, they appear attractive for use as oil-displacing media. If such fluids, however, are employed in formations which are shaley or have shale streaks, there is a tendency for the shales to interfere with the effectiveness and stability of the emulsions. This tendency can

be reduced through application of the present invention by controlling the vapor pressure of the aqueous phase of the emulsions or microemulsions so that it is substantially equal to or less than the aqueous vapor pressure of the shaley constituents of the formation. The manner of control is the same as that described for drilling fluids earlier in this disclosure. Since the vapor pressure of droplets of a liquid become significantly higher than the vapor pressure of the bulk liquid itself if the droplets are small enough, droplet diameter can be a design consideration in formulating microemulsion displacement fluids. Data on the effect of droplet diameter is presented by Paul Becher on page 8 of *Emulsions: Theory and Practice*, Reinhold Publishing Corporation, New York (1957).

C Fracturing Fluids

Many of the hydraulic fracturing fluids used to stimulate oil wells contain water. When such fracturing fluids are used in the presence of argillaceous, water-sensitive formations, the formations tend to swell and are thereby damaged. This damage can be prevented by using oil-base or water-in-oil invert emulsion fracturing fluids prepared in accordance with this invention. For fracturing fluids the amount of vapor pressure depressant added to the aqueous phase of the emulsion fluid should be sufficient to reduce the aqueous vapor pressure of the emulsion fluid to a level substantially equal to that of the water-sensitive formation. A particularly successful fracturing method which is described in U.S. Pat. No. 3,378,074 utilizes a viscous dispersion of water-in-oil as a fracturing fluid. The viscous fluid is lubricated down the borehole by means of an annular ring of water. Since the fracturing fluid and the annular ring are subjected to extreme turbulence as the combined stream is forced through perforations and into the formation to be fractured, it appears that at least temporarily both combine to form a water-in-oil emulsion. As a result, it is desirable to add a vapor pressure depressant to both the internal phase of the fracturing fluid and the water used to form the annular ring.

III General

It will be understood, and particularly so with respect to the claims which follow, that while numerous references are made herein to the aqueous activity, relative humidity or relative vapor pressure of materials, e.g., earth formations, samples of such formations and water-containing fluids, in each case the quantitative value referred to is the ratio of the aqueous vapor pressure of the material to the vapor pressure of water at the same temperature. This ratio is proportional to the aqueous vapor pressure of the material, can be measured rapidly and accurately and has proved to be a convenient quantitative value for characterizing the aqueous vapor pressures of material employed or acted upon in association with the methods of the invention. Along these same lines, it will also be understood that the aqueous vapor pressure relationships between well fluids and earth formations referred to herein refer to the aqueous vapor pressures of materials as they exist at downhole temperatures. Also, when the aqueous vapor pressure of an earth formation is mentioned it is assumed that the earth formation is at its natural state of hydration. A particular advantage in characterizing the aqueous vapor pressure of a material by its relative aqueous vapor pressure is the relative insensitivity of

the ratio to temperature when compared to the absolute aqueous vapor pressure. This is particularly advantageous where measurements are carried out on well fluids and formation samples in the laboratory or in the field at ambient conditions for the purpose of designing emulsion fluids for downhole conditions. That measurements of relative aqueous vapor pressure conducted at atmospheric conditions of temperature and pressure are very good approximations of downhole conditions has been demonstrated repeatedly by the excellent results achieved when using fluids designed by these techniques in actual well drilling operations.

What is claimed is

1 A method of drilling a well in a water-sensitive, argillaceous formation with a water-in-oil emulsion drilling fluid which comprises monitoring the aqueous vapor pressure of said drilling fluid during the drilling operation and maintaining an aqueous vapor pressure depressant in the aqueous phase of said drilling fluid in a concentration sufficient to substantially prevent migration of water from said fluid to said formation

2 A method as defined in claim 1 in which the aqueous vapor pressure of the drilling fluid is monitored by measuring the relative humidity of the atmosphere in contact with a sample of the drilling fluid

3 A method as defined in claim 1 in which said water-sensitive formation is an argillaceous hard shale formation

4 A method as defined in claim 1 in which a sufficient concentration of said aqueous vapor pressure depressant is maintained in the aqueous phase of said drilling fluid to render the aqueous vapor pressure of the drilling fluid about equal to the aqueous vapor pressure of said water-sensitive formation,

5 A method as defined in claim 4 in which said water-sensitive formation is an argillaceous hard shale formation

6 In a well operation in which a water-sensitive, argillaceous shale formation having a natural state of hydration is contacted with a water-in-oil emulsion fluid, the improvement which comprises maintaining the aqueous vapor pressure of said emulsion fluid at a value which will prevent a sample of said formation at said natural state of hydration from absorbing water from said emulsion fluid

7 A method as defined in claim 6 in which the earth formation is a hard shale

8 A method as defined in claim 6 in which the aqueous vapor pressure of said emulsion fluid is maintained at a value which will prevent migration of water between said sample and said emulsion fluid

9 A method of drilling a well through a subterranean, water-sensitive, argillaceous formation comprising determining the aqueous vapor pressure of a sample of said formation having substantially the same state of hydration as the natural hydration of said formation and drilling said formation with a water-in-oil emulsion drilling fluid having an aqueous vapor pressure substantially no greater than the aqueous vapor pressure of said sample

10 A method as defined in claim 9 in which the aqueous vapor pressure of said sample is determined by measuring the relative humidity of the atmosphere in contact with the sample

11 A method as defined in claim 10 in which said atmosphere in contact with said sample is in substantial equilibrium with said sample

12 In a method of drilling a well in a water-sensitive, argillaceous formation with a water-in-oil emulsion drilling fluid containing an aqueous vapor pressure depressant within the aqueous phase, the improvement which comprises measuring the degrees of attraction possessed by one or more samples of said formation for water in said emulsion fluid upon contact therewith and at different sample water contents, determining the concentration of aqueous vapor pressure depressant within said aqueous phase required to substantially prevent migration of water from said aqueous phase to a sample of said formation for a water content substantially equal to that of said formation, and drilling said formation with said emulsion fluid containing said required concentration of vapor pressure depressant in the aqueous phase thereof.

13. In a method of drilling a well in a water-sensitive, argillaceous shale formation with a water-in-oil emulsion drilling fluid wherein the aqueous vapor pressure of said drilling fluid is greater than the aqueous vapor pressure of said formation during drilling, the improvement which comprises adding a water soluble, aqueous vapor pressure depressant to said drilling fluid in a quantity sufficient to lower the aqueous vapor pressure of said drilling fluid to a value substantially equal to the aqueous vapor pressure of said formation

14 A method as defined in claim 13 in which said water-sensitive formation is an argillaceous hard shale formation

15 In a method of drilling a well in a water-sensitive, argillaceous shale formation with a water-in-oil emulsion drilling fluid wherein the aqueous vapor pressure of said drilling fluid during drilling is less than the aqueous vapor pressure of said formation, the improvement which comprises increasing the aqueous vapor pressure of said drilling fluid to a value substantially equal to the aqueous vapor pressure of said formation

16. A method as defined in claim 15 in which the aqueous vapor pressure of the drilling fluid is increased by adding water to the aqueous phase of said drilling fluid

17 In a method of drilling a well in a water-sensitive, argillaceous shale formation with a water-in-oil emulsion drilling fluid, the improvement which comprises maintaining an aqueous vapor pressure depressant in the water phase of the drilling fluid in a concentration sufficient to prevent the absorption of water by said water-sensitive formation from said drilling fluid

18. A method as defined in claim 17 in which said water-sensitive shale formation is a hard, argillaceous shale formation

19 In a method of drilling a well through a water-sensitive, argillaceous shale formation with a water-in-oil emulsion drilling fluid, the improvement which comprises maintaining the aqueous vapor pressure of said emulsion fluid at a value which will prevent the migration of water from said emulsion fluid to said formation.

20 A method as defined in claim 19 in which said formation is a hard shale

21 A method as defined by claim 19 in which the aqueous vapor pressure of said emulsion fluid is main-

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tained at a value which will prevent migration of water between said emulsion fluid and said formation

22 A method as defined in claim 21 in which said formation is a hard shale

23 In a method of drilling a well in a hard, argillaceous shale formation with a water-in-oil emulsion drilling fluid containing an aqueous vapor pressure depressant in the aqueous phase thereof, the improvement which comprises maintaining the aqueous vapor pressure of the drilling fluid at a level that is substantially no greater than the aqueous vapor pressure of said hard argillaceous shale formation.

24 In a method of circulating a water-in-oil emulsion fluid within a well in a water-sensitive, argillaceous shale formation having an aqueous activity less than 0.75, the improvement which comprises maintaining an aqueous vapor pressure depressant in the water phase of said fluid in a concentration such that the aqueous activity of said fluid is substantially equal to the aqueous activity of said formation

25 A method as defined by claim 24 wherein the aqueous vapor pressure depressant is calcium chloride and the aqueous activity of said formation is not substantially lower than 0.3

26 In a method of drilling a well through a hard, argillaceous shale formation having an aqueous activity less than 0.75, the improvement which comprises circulating a water-in-oil emulsion drilling fluid within said well, said drilling fluid having an aqueous activity about equal to that of said formation

27 A method as defined in claim 26 wherein the aqueous activity of said shale formation is not substantially lower than 0.3 and the aqueous phase of said drilling fluid is an aqueous solution of calcium chloride

28 In a method of drilling a well through a water-sensitive shale formation with a water-in-oil emulsion drilling fluid, the improvement which comprises determining the type and concentration of an aqueous vapor pressure depressant required in the aqueous phase of said emulsion fluid to prevent said formation from withdrawing water from said emulsion fluid and maintaining the concentration of said aqueous vapor pressure depressant in the aqueous phase of said emulsion fluid at a level substantially no lower than said required concentration

29 The method of claim 28 wherein said aqueous vapor pressure depressant is a water-soluble salt.

30 The method of claim 29 wherein said aqueous vapor pressure depressant is sodium chloride

31 The method of claim 29 wherein said aqueous vapor pressure depressant is calcium chloride

32 In a method of drilling a well through a water-sensitive shale formation with a water-in-oil emulsion drilling fluid, the improvement which comprises determining the type and concentration of an aqueous vapor pressure depressant required in the aqueous phase of said emulsion fluid to prevent migration of water between said emulsion fluid and said formation and maintaining the concentration of said aqueous vapor pressure depressant in the aqueous phase of said emulsion fluid at a level substantially no lower than said required concentration

33 The method of claim 32 wherein said aqueous vapor pressure depressant is a water-soluble salt.

34 The method of claim 33 wherein said aqueous vapor pressure depressant is sodium chloride

35 The method of claim 33 wherein said aqueous vapor pressure depressant is calcium chloride

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UNITED STATES PATENT
Chenevert

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[54] OIL RECOVERY PROCESS

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Related U.S. Application Data

- [63] **Continuation-in-part of Ser No. 726,693, May 6, 1968, abandoned, which is a continuation-in-part of Ser Nos. 675,490, Oct. 16, 1967, abandoned, and Ser No. 699,255, Jan. 19, 1968, abandoned.**
[52] **U.S. Cl. ..** **166/252, 166/275, 166/305 R, 166/308**
[51] **Int. Cl.** **E21b 43/12, E21b 43/25, E21b 43/26**
[58] **Field of Search ..** **.. 166/252, 268, 273-275, 166/305 R, 308, 252/8.55 D**

[56] References Cited

UNITED STATES PATENTS

- 3,254,714 6/1966 Gogarty et al - ..166/274
3,123,133 3/1964 Bernard et al ..166/275 X

- 3,149,669 9/1964 Binder et al 166/275 X
3,208,528 9/1965 Elliott et al ... 166/305 R

OTHER PUBLICATIONS

Moore, John E. How to Combat Swelling Clays, in Petroleum Engineer, Mar 1960, pp B- 78,- 90,- 94,- 95,- 96,- 98 through- 101

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[57] ABSTRACT

A method of displacing oil from a subsurface, water-sensitive, oil-bearing formation is disclosed. The new method involves determining the aqueous vapor pressure of the water-sensitive formation and injecting into the formation through an input well an oil-continuous displacement fluid having water dispersed therein which fluid has an aqueous vapor pressure no greater than that of the formation, and recovering oil displaced thereby from the formation at a point removed from the point of injection.

13 Claims, 8 Drawing Figures

PATENTED JUN 20 1972

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SHEET 1 OF 5

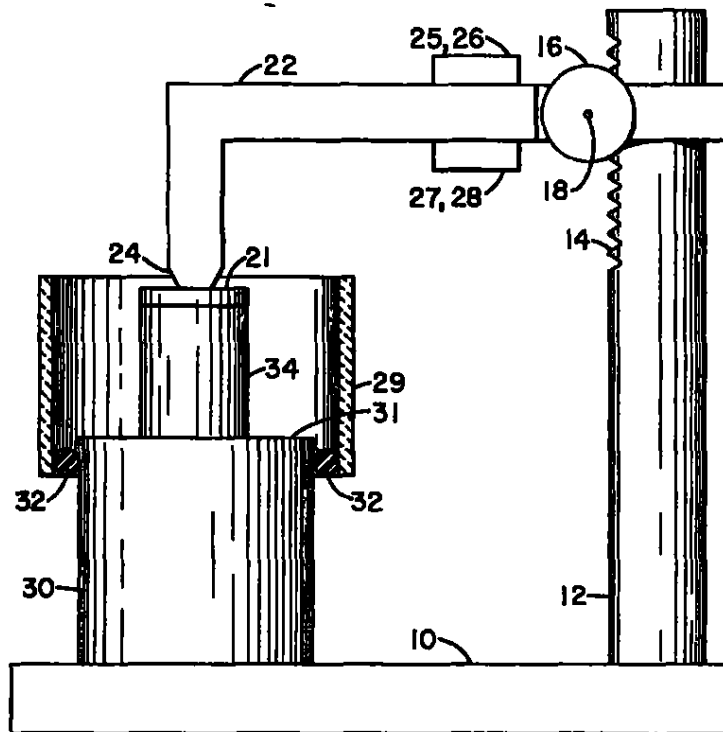


FIG. 1

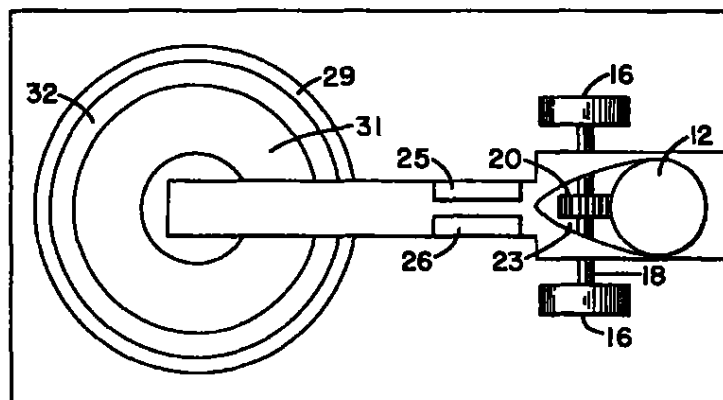


FIG. 2

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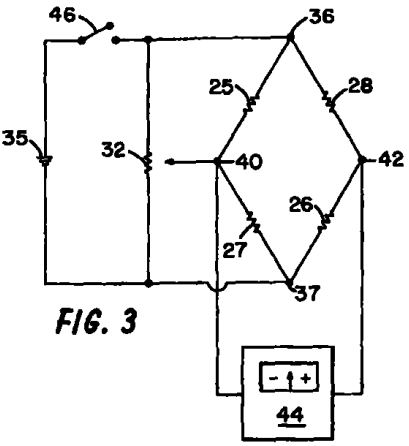


FIG. 3

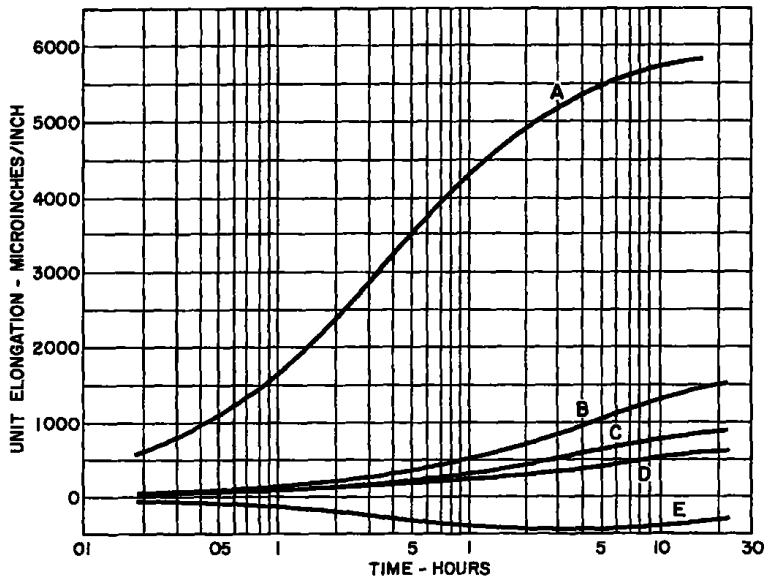


FIG. 4

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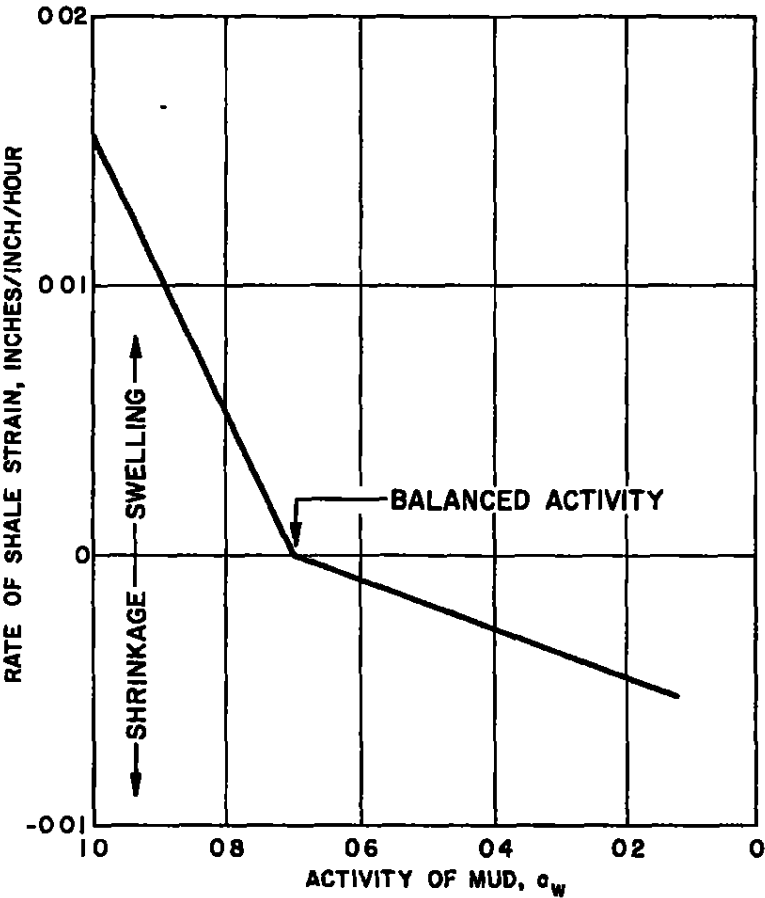


FIG. 5

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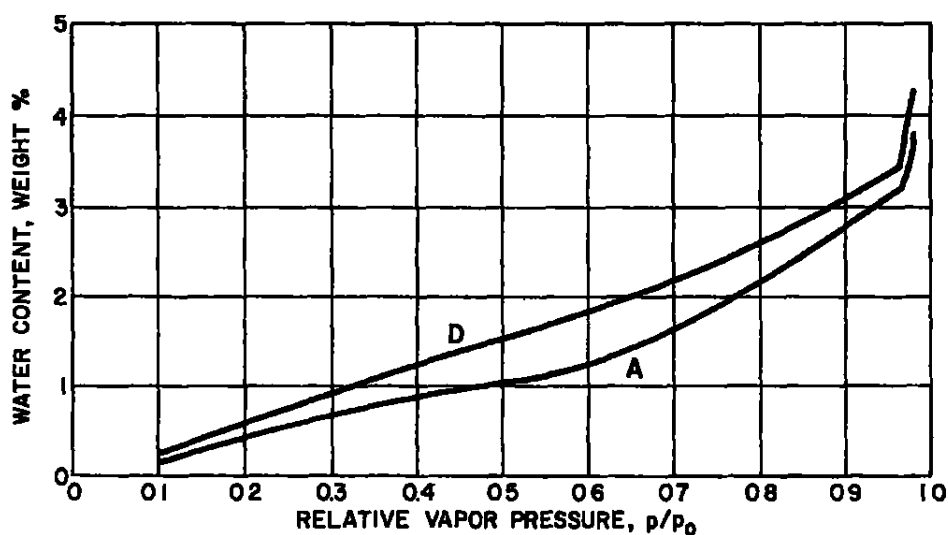


FIG. 6

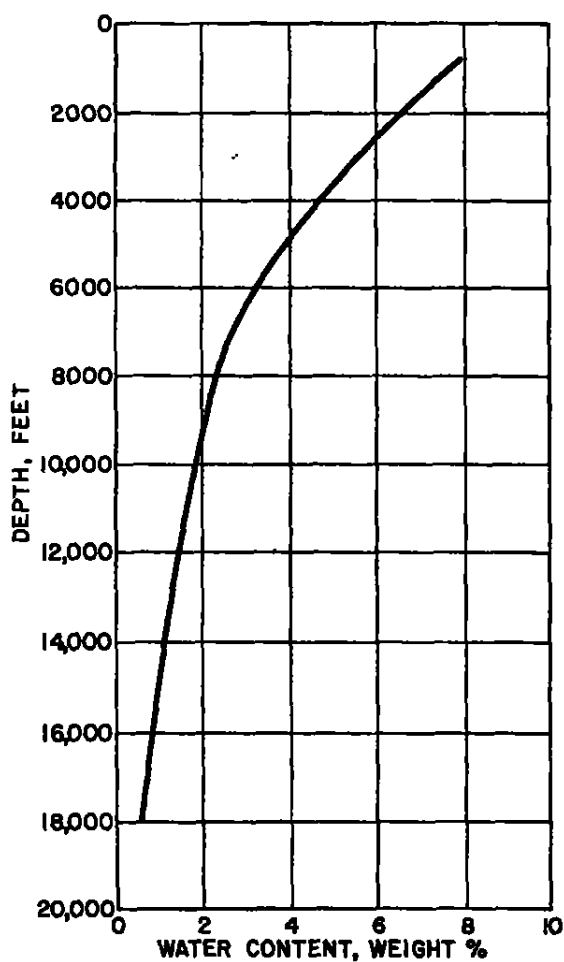


FIG. 7

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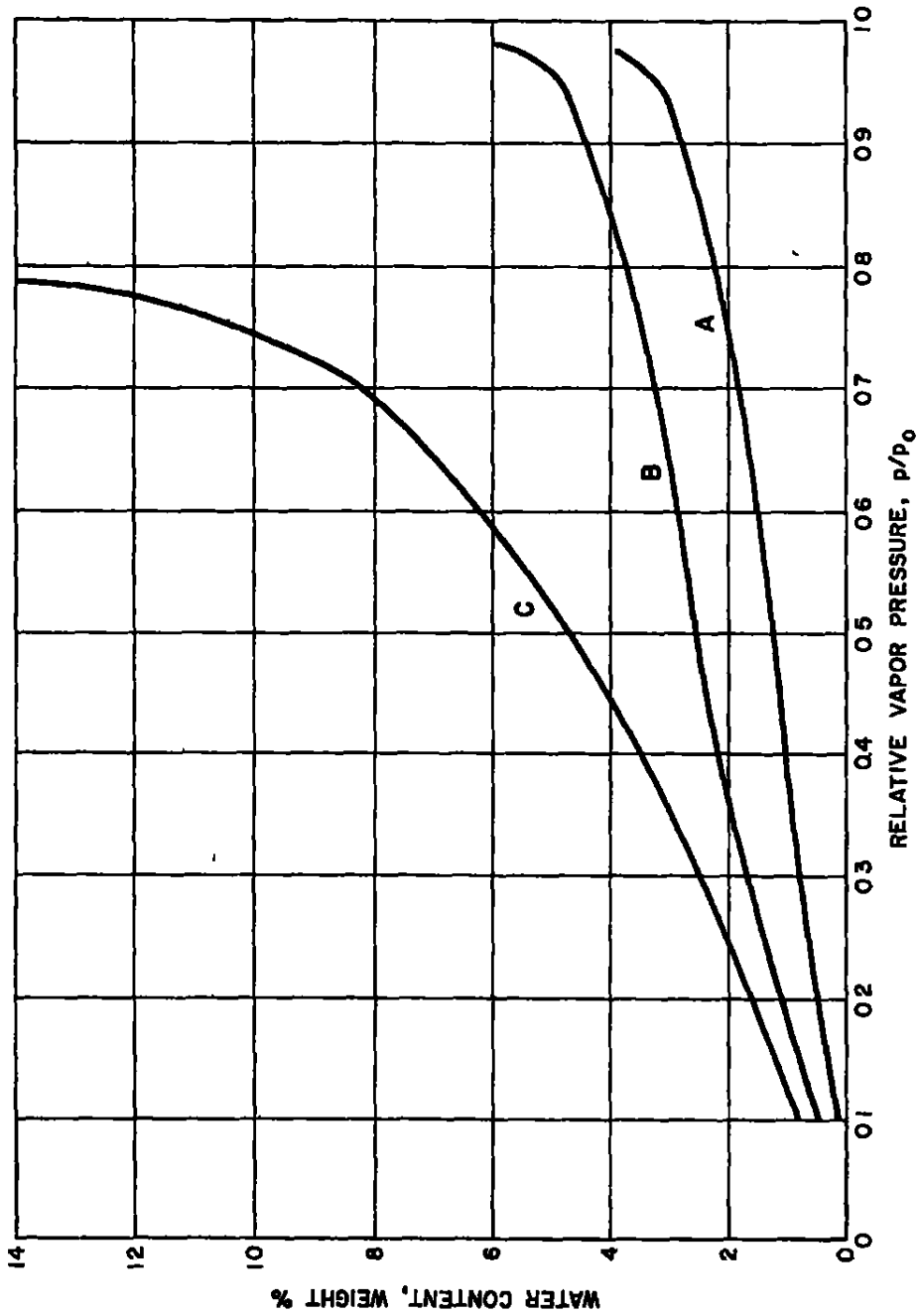


FIG. 8

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OIL RECOVERY PROCESS

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application, Ser No. 726,693, filed May 6, 1968, now abandoned, which in turn was a continuation-in-part of application, Ser No. 675,490, filed Oct. 16, 1967 and application, Ser No. 699,253, filed Jan. 19, 1968, both now abandoned. It is also based in part on pending application, Ser No. 19,574, a continuation-in-part of application, Ser No. 726,693, filed Mar 16, 1970.

BACKGROUND OF THE INVENTION

1 Field of the Invention

This invention is directed to methods for displacing oil from a subsurface, water-sensitive, oil-bearing formation with an oil continuous displacement fluid having water dispersed therein.

2 Description of the Prior Art

Additional recovery techniques involving the displacement of crude oil from subsurface earth formations by injecting a displacing fluid into the formation through an input well and recovering oil displaced from the formation thereby at a point removed from the point of injection have been in use by the petroleum industry for a number of years. These displacement processes normally involve injecting a quantity of a displacing fluid into a permeable, oil-bearing formation at a pressure sufficient to displace recoverable oil contained within the interstices of the formation. Injection operations are normally continued until a substantial percentage of the produced fluid is comprised of the displacing fluid. The use of these displacement processes as a supplement to or following primary oil recovery frequently results in substantial increases in the overall recovery of crude oil from productive formations.

A number of problems are encountered in displacement operations which are conducted in water-sensitive formations. The nature and extent of the difficulties encountered are dependent upon the characteristics of the particular reservoir rock to be flooded and are particularly acute where the formations contain argillaceous materials. When argillaceous material is contained in the reservoir rock, the introduction of water into the formation frequently results in swelling of the argillaceous material which in turn causes a reduction of matrix permeability. This permeability reduction caused by clay swelling may significantly impair the effective permeability of the reservoir rock, thereby reducing injectivity and rendering displacement operations much more difficult. It is therefore desirable that the displacement fluids which contact the clay-containing rock matrix not cause clay swelling with attendant reduction in permeability of the formation.

It is known for instance that employing fresh water as a displacement fluid where the producing formation contains montmorillonite or other hydratable clays results in clay swelling. Accordingly, it has been suggested that water-sensitive formations be flooded with brines or with fluids having oil as the external phase to prevent the argillaceous materials from swelling. The oil external fluids frequently include dispersions of water in oil as for example water-in-oil emulsions. A large number of additives have been employed in conjunction with these oil-continuous displacement fluids which contain dispersed water, including the addition of various electrolytes to the aqueous phase for a variety of reasons. The problems caused by swelling of argillaceous materials, despite the use of oil continuous fluids have, however, heretofore persisted. There therefore exists a need for a method of designing a displacement fluid that will not result in reduction of matrix permeability in water-sensitive formations caused by swelling of argillaceous materials.

SUMMARY OF THE INVENTION

The present invention provides means for alleviating the problems normally encountered when water-sensitive argillaceous earth formations are contacted with aqueous fluids. The invention greatly improves the performance of oil-con-

tinuous displacement fluids and, while described herein primarily in relation to the drilling of water-sensitive formations, its applicability to displacement operations will be apparent to those skilled in the art.

In accordance with the invention, it has now been found that shales, shaly sands, and similar argillaceous formations, in spite of their extremely low permeability, possess a strong attraction for water and are capable of withdrawing water from water-in-oil emulsions and other fluids with which they come in contact. This sensitivity to water is evidenced by dimensional changes in response to the absorption or desorption of water. These changes, although sometimes very slight, contribute materially to formation failure. It has been found that the rate at which such a formation withdraws water from a particular aqueous fluid is a quantitative measure of the degree of water sensitivity of the formation in the presence of that fluid. This rate and hence the water sensitivity of the formation can be assessed by at least partially immersing a substantially unaltered sample of the formation in the fluid and measuring the changes in dimensions, weight, or other properties of the sample, directly or indirectly, over a selected period. A preferred method of measuring the water sensitivity of the formation is to measure the deformation rate, whether visible or subvisible, of a formation sample in the presence of the fluid.

Although the mechanisms responsible for the transfer of water between the emulsion fluid and the argillaceous shale with which the emulsion fluid comes in contact are evidently complex and are not fully understood, experience has shown that water transfer from the emulsion fluid to the shale will normally occur if the vapor pressure of the aqueous phase of the fluid is greater than the vapor pressure of the formation. Measurement of vapor pressures thus provides a convenient technique for the evaluation of emulsion fluids. Aqueous vapor pressure is directly proportional to the activity of water and hence water transfer will normally occur from emulsion to shale when the activity of the water contained within the aqueous phase of the emulsion exceeds that of water contained within the shale. It is important to note that the aqueous vapor pressure of the formation normally differs from the vapor pressure of the water or brine contained within the formation. It appears that certain electrical or absorptive forces associated with the matrix or composition of the formation itself greatly decrease the vapor pressure which the water contained therein would otherwise be expected to have. Measurement of the aqueous vapor pressure of the formation which characterizes the activity of the formation water, is therefore an important aspect of the invention.

Two general methods for designing oil-base drilling fluids in accordance with the invention are disclosed. Both involve the addition of vapor pressure depressants to the aqueous phase of the emulsion fluid in amounts sufficient to eliminate or to retard transfer of water from the drilling fluid to the argillaceous formation. The first method is a direct simulation of the interaction of the fluid and the water-sensitive formation. A water vapor pressure depressant is preferably first dissolved in the aqueous phase of the emulsion drilling fluid. The rate of water transfer between this fluid and the formation is then quantitatively determined by immersing a sample of the formation in substantially its natural state in the fluid and determining the rate of deformation. The concentration of the water vapor depressant can then be increased and additional samples tested until a concentration that reduces the rate of deformation to substantially zero is found. A deformation rate that for all practical purposes approaches zero indicates that the fluid can be used with little likelihood of damaging the formation.

A second method for designing drilling fluids requires that the aqueous vapor pressure for the argillaceous shale formation first be determined. This can be done by exposing formation samples to atmospheres above different saturated salt solutions having known water vapor pressures until equilibrium is reached. By observing the weight change of the sample

resulting from water migration, the vapor pressure of an atmosphere that would result in no weight change is determined. This value represents the formation vapor pressure. After thus determining the vapor pressure of the shale formation, an emulsion fluid having an aqueous vapor pressure substantially equal to that of the formation can be prepared. Such a fluid can be used to drill the water-sensitive formation with little likelihood of the hole sloughing.

It is still a further aspect of the invention to provide an improved method of displacing oil from water-sensitive earth formations. The improved method comprises determining the aqueous vapor pressure of the water-sensitive formation and injecting into the formation through an input well an oil-continuous displacing fluid having water dispersed therein in which the fluid has an aqueous vapor pressure no greater than that of the formation, and recovering oil displaced thereby from the formation at a point removed from the point of injection. By maintaining this relationship between the aqueous vapor pressure of the formation and of the displacement fluid, migration of water from the fluid to the argillaceous formation is prevented, eliminating swelling of the argillaceous material in the matrix and resultant permeability reduction. The displacement method of the present invention will thus be seen to have significant advantages over techniques available heretofore.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG 1 schematically depicts an elevation view of a displacement transducer instrumented with strain gauges suitable for performing the simulation test method of the invention.

FIG. 2 is a schematic plan view of the apparatus of FIG 1

FIG. 3 is a schematic diagram of an electrical circuit that can be used with the apparatus of FIG 1

FIG 4 graphically illustrates unit elongation versus log time data recorded while testing a hard shale in accordance with the simulation test method of the invention.

FIG 5 graphically illustrates the rate of deformation exhibited by a number of samples of an argillaceous shale formation contacted by water-m-oil emulsion drilling fluids having different aqueous activities.

FIG 6 shows the water vapor pressure (P), relative to the vapor pressure of pure water (P_w), exhibited by a West Texas hard shale at 25° C for various water contents within the shale

FIG 7 is a correlation showing the average variation in the water content of a shale in terms of depth of burial within the earth

FIG 8 is a correlation showing the average vapor pressure (P) of two hard shales and one soft shale relative to the vapor pressure of pure water (P_w) at 25° C for different shale water contents.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

I. Design of Drilling Fluids

A. The Simulation Test Method

1. Nature of the Simulation Test Method

The simulation test is based on the discovery that the rate at which shales and other argillaceous formations absorb water from a particular aqueous fluid is a quantitative measure of the degree of water sensitivity of the formation in the presence of the fluid. The test is performed by at least partially immersing a sample of the formation which is in substantially its natural state of hydration in the drilling fluid of interest and determining the rate of water absorption.

One method for determining the water absorbed is by change of weight of the sample. The sample is weighed initially and its change in weight observed over a period of time. Any change in weight which occurs is attributable to the migration of water. Weight measurements can be obtained while the sample is immersed by suspending it in the drilling fluid and periodically recording the suspended weight. In lieu of this, the sample may be withdrawn from the fluid after a

fixed period of time, cleaned, and then weighed. Another method recognizes that the resistivity of the sample will decrease as it absorbs water and utilizes changes in resistivity to measure the amount of water absorbed. Still other methods are based on the measurement of changes in sonic velocity, compressive strength, and other physical properties which vary with water content to indicate the rate of absorption.

The preferred method of measuring absorption is to log the rate of change in dimensions of a shale sample while it is immersed in the drilling fluid. This gives a direct measurement of the deformation of the shale due to the drilling fluid and thus provides a quantitative measurement of the rate of water absorption. A wide variety of devices for recording changes in dimensions may be used, including micrometers, optical equipment, dial displacement indicators, and the like. The preferred apparatus, however, is a displacement transducer instrumented with strain gauges.

2. The Displacement Transducer Apparatus

FIGS. 1 and 2 illustrate a resistance strain gauge displacement transducer suitable for measuring the change in dimensions of a sample of shale or similar material. This apparatus includes a rectangular base 10 from which a substantially cylindrical column 12 extends vertically. A series of beveled teeth on the upper portion of column 12 form rack 14.

Caniliver deflection beam 22 engages rack 14. The outermost end of the deflection beam extends downwardly in an L-shape terminating in a frusto-conical end terminus 24. Contact shoe 21 is mounted on end terminus 24. The innermost end of the deflection beam 22 contains a generally oval aperture 23, one end of which forms a yoke that fits over upright column 12 and forms a slidable support with the column. Shaft 18 passes through deflection beam 22 at the other end of aperture 23. Knobs 16 are mounted on the ends of shaft 18. Pinion 20 is supported on the shaft 18 in a position corresponding to the middle of the aperture to cooperate with rack 14. Upper strain gauges 25 and 26 are mounted on the upper side of deflection beam 22. Lower strain gauges 27 and 28 are positioned on the other side of the beam.

A cylindrical pedestal 30 extends from a rectangular base 10 underneath contact shoe 21. The upper surface 31 of the cylindrical pedestal is smooth and forms a bearing surface underneath shale sample 34. Cylindrical cup 29 slides upon cylindrical pedestal 30. Sealing member 32 is mounted between the cup and the pedestal to prevent the leakage of fluid.

FIG 3 illustrates an electrical circuit suitable for use with the strain gauge displacement transducer apparatus. A four-resistor electrical bridge in which strain gauges 25, 26, 27, and 28 form the resistors is shown. At least four resistors are generally used to obtain increased amplitude and inherent temperature compensation. Variable resistor 32 is placed in the circuit to balance the bridge prior to strain measurements. Voltage source 35 creates a difference in potential across resistor 32 and across the bridge between contacts 36 and 37, causing direct current to flow through resistor 32 and the legs of the bridge formed by resistors 25 and 27, and 26 and 28, respectively. Voltage is measured between terminals 40 and 43 by voltmeter 44. In lieu of this, a suitable strain indicator, such as Model P-350 sold by The Budd Company, Phoenixville, Pennsylvania, could be used. Switch 46 is used to turn the strain gauge transducer on and off. Although the relatively simple strain gauge circuit illustrated is suitable, other circuits such as those illustrated in M. Hetenyi's book, *Handbook of Experimental Stress Analysis*, John Wiley & Sons, Inc., New York, New York (1950) could readily be adopted.

Prior to using the strain gauge transducer, it must be calibrated to determine the relationship between observed voltages and displacement. This can be done by first zeroing the voltmeter, as is discussed below, and then placing successively larger or smaller articles of known length between contact shoe 21 and cylindrical pedestal 30 and observing the voltages. From these data a constant that relates voltage and displacement can be obtained.

To use this equipment to analyze the compatibility of a drilling fluid and a particular shale, a sample of the shale should be placed on surface 31 of cylindrical pedestal 30. Deflection beam 22 is then lowered by turning knob 16. This rotates shaft 18 on which pinion 20 is mounted. Pinion 20 cooperates with rack 14 to convert the rotational movement of the knob 16 into a downward translational movement of beam 22. The beam should be lowered until contactor shoe 21 engages the shale sample 34 and holds it firmly in place on surface 21 of the pedestal 30.

With the shale sample thus mounted, the strain gauge's electrical circuit should be balanced. Voltage source 35 is energized by closing switch 46, causing current to flow through variable resistor 32 and both sides of the resistance bridge. The bridge is balanced by adjusting variable resistor 32 until voltmeter 44 is zeroed. Once the bridge has been balanced, the voltage readings will indicate deformation. Cylindrical cup 29 is then raised to its uppermost position so that the upper edges of the cup are above the top of sample 34. Sufficient drilling fluid to cover the sample is then poured into the cup held between contactor shoe 21 and surface 31 of cylindrical pedestal 30.

Once the drilling fluid contacts the sample mounted within the strain gauges, the sample will begin to absorb water and expand if it is incompatible with the fluid. Expansion of the sample will force contactor shoe 21 upward, deflecting beam 22. Deflection of the beam results in deformation of the strain gauges and produces an imbalance in voltage readings across the bridge. If the fluid absorbs water from the sample, the sample will generally exhibit shrinkage. Such shrinkage also normally produces an imbalance in voltage readings across the bridge. However, these voltages will have an opposite sign from those caused by swelling.

Several voltage readings should be taken at various times after the sample has been immersed in the drilling fluid. The voltage readings are proportional to the displacement of the sample between contactor shoe 21 and pedestal 30. The relationship between displacement and time can be determined from the calibration constant and used to determine the rate at which the sample will absorb water from the particular drilling fluid. When comparing data, it is useful to normalize the displacement data by dividing each reading by the sample length. The normalized data is then referred to as "strain." The rate so determined is indicative of the degree of compatibility between the water-sensitive formation and the drilling fluid.

3 Selection and Preparation of Formation Samples

The determination of the water sensitivity of a subsurface formation in the presence of a particular drilling fluid in accordance with the invention is normally carried out with a sample of the formation having substantially its in situ composition. Exposure to high temperatures and other treatment that may alter the composition should be avoided. It is preferred that this sample be in substantially its natural state of hydration so that its surface absorption behavior will approximate in situ absorption behavior. Laboratory tests performed at reservoir conditions of temperature and pressure, when compared with absorption tests conducted under atmospheric conditions, indicate that atmospheric tests are sufficiently accurate for most practical purposes.

The formation samples utilized may be preserved core samples from the subject well or from a nearby well that penetrates the same formation. Such preserved samples are particularly representative when the coring fluid used inhibits absorption of water by the water-sensitive formation. Fragments of the formation entrained by the drilling fluid and carried to the surface can also be used. Since a water-sensitive formation will begin hydration as soon as it is contacted with a water-containing drilling fluid, it is preferable that such fragments be recovered as early as possible after initial contact of the rock by the fluid. Hence, the depth of the formation of interest should be estimated and samples from the earliest returns from drilling the formation should be secured for the

test. The use of an oil-base drilling fluid treated in accordance with the invention generally simplifies the recovery of samples in substantially their natural state of hydration.

Where severe hydration of the formation has occurred, the samples obtained should be restored to their natural state of hydration. Hydration is not always encountered when the drilling fluid is a treated oil-base fluid and is generally more severe where a water-base fluid is used to drill a highly water-sensitive shale. Restoration to a substantially natural state can be accomplished by baking the samples at a temperature slightly above 100° C. until sample density corresponds with typical shale density for this formation and depth of burial. Sample density can be rapidly determined by means of a graduated density liquid column, the mercury pump pressure chamber method, or other suitable techniques. Correlations of shale density versus depth of burial are available in the literature for various formations and are typified by those published by K. F. Dallmeyer in his study "Mechanics of Basin Evolution and Its Relation to the Habitat of Oil in the Basin," *Habitat of Oil - A Symposium*, Tulsa, Amer. Assoc. Petrol. Geol., 1958, p. 883-931. It is important that temperature not greatly exceed 100° C. since excessive temperatures may result in substantial changes in characteristics of the sample.

4. Drilling Fluid Design

Use of the method and apparatus of the invention to formulate an oil-base drilling fluid that will prevent or minimize absorption and thus promote borehole stability is based in part on the observation that an oil-base or water-in-oil emulsion mud having an aqueous vapor pressure substantially equal to or less than that of the troublesome water-sensitive formation will prevent absorption of water by the formation. Samples of the water-sensitive formation in substantially their natural state should be used, as indicated above. Several of these samples are preferably immersed in a corresponding number of different oil-base drilling fluids having different aqueous vapor pressures and strain-time data are obtained for each formation combination. This procedure can be greatly expedited by using a number of strain gauge displacement transducers.

A series of water-in-oil emulsions or other oil-base muds having different aqueous vapor pressures can be prepared by adding various concentrations of inorganic salts such as NaCl or CaCl₂ to the mud. A number of other vapor pressure depressants are discussed herein in connection with the method of determining the vapor pressure of an earth formation. Suitable vapor pressure depressants are not limited to these or similar inorganic salts, however. Any solute introduced into the aqueous phase will reduce the aqueous vapor pressure.

FIG. 4 illustrates strain-time data obtained in accordance with the invention for the hard, argillaceous Wolfcamp shale. Fluid A is water, and the high rate of absorption for this fluid is typical of a very compatible fluid. Fluids B, C, D, and E are water-in-oil invert emulsions containing in the aqueous phase, as vapor pressure depressants, 130,000-ppm NaCl, 200,000-ppm NaCl, 270,000-ppm NaCl, and 450,000-ppm CaCl₂, respectively. Curves B, C, and D illustrate the reduction in absorption that occurs as the concentration of the aqueous vapor pressure depressant is increased and the aqueous vapor pressure of the fluid approaches that of the formation. Curve E illustrates behavior characteristic of a water-in-oil emulsion mud with an aqueous vapor pressure that has been reduced below that of the water-sensitive formation. Instead of swelling, the shale sample shrinks, indicating that water is being desorbed from the shale sample. The use of a drilling fluid with a composition similar to that of mud E would therefore prevent absorption of water by the shale. Generally, however, there is little incentive in attempting to dehydrate a water-sensitive formation and therefore such a fluid would normally be considered to contain an excessive amount of vapor pressure depressant. In most cases it would be more economical to reduce the concentration of CaCl₂ in Fluid E so that its strain-log-time curve would more closely approach the zero strain line than to use a mud such as Fluid E.

FIG 5 illustrates graphically the rates of deformation of a series of shale samples exposed to invert muds having varying aqueous activities (relative vapor pressures). The shale formation on which the tests were run had an aqueous activity of 0.7. Each test involved immersing a shale sample in an invert mud having a known aqueous activity for a period of 10 hours, measuring the strain, and then computing the average rate of strain of the sample over this time period. It will be noted that shale samples exposed to muds having aqueous activities higher than 0.7 swelled and that the observed rate of swelling increased as the difference in aqueous activity between the mud and the sample increased. Samples contacted with muds having aqueous activities lower than 0.7 shrank. Again, however, the rate of deformation increased in relation to the activity difference. These data demonstrate that when a difference in activity exists, water will flow either from the emulsion mud to the shale or from the shale to the mud. The former causes swelling of the water-sensitive subterranean formation, leading to its sloughing into the wellbore; the latter increases the water content and thus viscosity of the drilling fluid, necessitating frequent additions of oil, salt, and other materials required to maintain the drilling fluid. However, when the activity of the mud is substantially equal to that of the shale formation being drilled, a unique relationship exists. So long as this balanced condition is maintained, there is substantially no migration of water in either direction. Thus, it is especially desirable to maintain the aqueous activity of the mud about equal to that of the shale and thereby both eliminate sloughing of the borehole and obviate the addition of salt, oil or other materials to the mud normally required when it is contaminated by water.

Although the emulsion test has been discussed in relation to water-in-oil emulsion drilling fluids the utility of the emulsion test is not limited to this type of drilling fluid. The emulsion test method and apparatus can be used to determine the compatibility of any drilling fluid with a water-sensitive formation and can be employed to select the most compatible drilling fluid from any group of drilling fluids. The method and apparatus can also be used to determine whether or not a particular formation is water-sensitive and to select fluids for use in secondary recovery, well stimulation, or other well operations, as is more fully discussed subsequently herein.

B The Formation Vapor Pressure Test Method

1 The Method of Determining the Vapor Pressure of an Earth Formation

The aqueous vapor pressure of a shale or other water-containing earth formation can be determined by subjecting a sample of the formation to air of a constant known humidity for a period of time sufficient for moisture within the shale to reach equilibrium with the moisture in the air. It will normally be difficult to preselect a humidity condition such that the natural water content of the shale will be in equilibrium with this condition of humidity. So, generally speaking, several different humidity conditions must be used to obtain a range of water contents within the sample which will span the in situ water content of the formation within the earth.

A very convenient procedure for exposing samples of a given formation to air of different humidities is to suspend or place the sample in a sealed container in an atmosphere of air above a saturated aqueous solution of a solute which contains an excess of undissolved solute. Thus, it is known that the relative humidity of the enclosed space above such a solution where the sample has been placed will remain substantially constant at a given temperature — conveniently room temperature (25° C). An article containing an explanation of this principle and also listing a number of saturated solutions and solutes is contained in Ecology Vol. 41, No. 1, pp. 232-237 Jan., 1960. Typically, a series of several different saturated solutions can be prepared, and one or more samples of a given shale or other formation can be exposed to an enclosed atmosphere above each of these samples for a sufficient period of time for equilibrium to occur. Complete equilibrium will normally take about 1 or 2 weeks, but substantial equilibrium can normally be attained in about 1 or 2 days.

As noted above, a number of different saturated aqueous solutions should be selected such that a given formation sample is equilibrated at a range of relative humidities. The use of 8 to 10 different relative humidities ranging from about 10 percent relative humidity to 95 percent or more relative humidity has been found to be very desirable and effective. In this connection, it has been found to be quite effective to use the following saturated solutions to obtain a suitable range of atmospheres. The solutions and the relative humidities which exist above these solutions are listed below:

Saturated solution of	Relative humidity (%) at 25° C
15 ZnCl ₂ 1 1/4 H ₂ O	10.0
CuCl ₂ 6H ₂ O	29.5
Ca(NO ₃) ₂ 4H ₂ O	30.5
NH ₄ Cl + KNO ₃	71.2
(NH ₄) ₂ SO ₄	80.0
20 Na Tartrate	92.0
KH ₂ PO ₄	96.0
K ₂ Cr ₂ O ₇	98.0

Many of these salts, incidentally, may themselves be used within the aqueous phase of invert emulsions for the purpose of establishing the vapor pressure of that phase. If vapor pressures less than that obtainable for a saturated calcium chloride solution are desired, solutions of ZnCl₂ 1 1/4 H₂O; LiCl H₂O; ZnBr₂ LiBr 2H₂O; potassium hydroxide or other stronger vapor pressure depressant may be employed. The depressant, of course, must be compatible with the invert emulsion of interest; and such compatibility should be tested prior to actual use.

After a formation sample has reached equilibrium with a particular atmosphere of known relative humidity, the sample should be withdrawn from the atmosphere and its water content promptly determined. A simple procedure for determining its water content is to weigh the equilibrated sample, and then repeat the weighing after the sample has been dried at about 105° C. for a period of 12 to 24 hours. The loss in weight of the sample is a direct measure of the equilibrated water content of the sample. The vapor pressure of the sample for this water content is the vapor pressure of water at room temperature (or the temperature of the equilibrium condition) multiplied by the percent relative humidity of the air in equilibrium with the sample.

After the vapor pressures and water contents of a given sample or set of samples have been determined, these values can be recorded on a suitable chart or other record medium and intermediate values can be determined from the resulting correlation. Thus, FIG 6 of the drawing shows two correlations ("A" for absorption conditions, and "D" for desorption conditions) obtained by subjecting samples of a West Texas hard shale to eight different conditions of relative humidity ranging from 10 percent relative humidity to 98 percent relative humidity at a temperature of 25° C. These curves also apply for temperatures at least as high as 100° C. As can be seen, slightly different correlations were obtained for tests in which water was desorbed from the shale samples as compared with tests in which water was absorbed by the shale samples. The shale sample in this instance had an in situ water content of 2.22 weight percent as determined by analyzing a small central portion of a core cut directly from the formation under conditions such that the water content of most of the core was undisturbed. From FIG 6, it is apparent that this formation has a water vapor pressure (for "formation vapor pressure") relative to the vapor pressure of pure water of between about 0.71 and 0.81.

Another convenient method for determining the aqueous vapor pressure of a water-sensitive formation is to place a sample that is representative of the subsurface formation in a sealed container until it reaches equilibrium with the enclosed atmosphere. A direct measurement of the relative humidity of the formation sample can then be made. This method is also

useful for determining the aqueous vapor pressure of a water-containing oil-base drilling fluid. Apparatus for measuring relative humidity is widely available. Typical of such apparatus is the Catalog No. 2200 ELECTRO-HYGROMETER that is sold by Lab-Line Instrument, Inc., Melrose Park, Illinois.

2 Selection and Preparation of Samples

As indicated earlier, the use of this invention in designing well fluids should be preceded by a determination of the vapor pressure characteristics of the portions of the zones or formations which the emulsion fluid will contact. In the case of a drilling operation, as pointed out earlier in the discussion of the simulation test, a sample of the formation of interest should be obtained so that its vapor pressure can be determined. If a sample of the formation is not obtainable directly from the well being drilled, then an effort should be made to obtain a sample from a nearby well. It is also possible, however, to collect and use cuttings from the well which is being drilled.

Again, the preferred type of formation sample to obtain and study is a sample from the central portion of a core which has been cut from the formation under conditions suitable to preserve the natural conditions of the core as much as possible. If such a sample is available, a reasonably accurate determination can be made of the amount of in situ water contained in the core. If such a core cannot be obtained, the formation's content can be estimated from FIG. 7. FIG. 7 is a correlation showing how the water content of many shaley formations within the earth vary, on the average, with increasing depth of burial. Thus, if a given formation lies about 10,000 feet beneath the surface, it may be expected to have, on the average, a water content of about 2 weight percent. It is then possible to use this water content, in combination with the method described earlier for determining the vapor pressure of a formation within the earth, to arrive at an approximate value of the vapor pressure possessed by the formation in its natural condition within the earth.

3 Drilling Fluid Design

Once the formation vapor pressure is known, it is then possible to select and formulate a water-in-oil drilling fluid having an aqueous phase vapor pressure which bears a particular relation to the aqueous vapor pressure of the formation. Generally speaking, it is desirable that the aqueous phase of the drilling fluid have an aqueous vapor pressure no greater than that of the water-sensitive formation. This frequently requires the aqueous vapor pressure of the drilling fluid to be less than that of a saturated sodium chloride solution and often it is desirable to saturate the aqueous phase of the drilling fluid with calcium chloride. As pointed out above with respect to drilling fluid design by the simulation method, it is especially desirable to maintain the aqueous activity of the mud at a level about equal to that of the water-sensitive formation. Balancing the activities in this fashion eliminates any substantial migration of water between the emulsion fluid and the formation, thereby eliminating any sloughing of the borehole as well as contamination of the mud by water contained within the shale.

However, economics or other considerations may occasionally make it undesirable to attempt to completely reduce the aqueous vapor pressure of the drilling fluid to that of the formation. As long as the water transfer between the fluid and formation is insufficient to cause excessive formation failure during the time period the water-sensitive formation is exposed to the wellbore, the aqueous vapor pressure of the drilling fluid can be considered to be substantially equal to that of the water-sensitive formation. However, it is preferable to reduce drilling fluid vapor pressure to a level that is equal to or below that of the formation.

It should be noted that mixtures of salts can be used in the water phase of an invert, but such mixtures are subject to the common-ion effect. Their aqueous solutions may thus have higher aqueous vapor pressures than would otherwise be suggested by the total salt concentration. It should also be noted

that the emulsifier and other water-soluble constituents of the drilling fluid may tend to slightly alter the vapor pressure of the aqueous solution containing the vapor pressure depressants when the emulsion fluid is prepared. Thus the aqueous vapor pressure of the emulsion fluid, which is the aqueous vapor pressure of the water phase of the emulsion fluid, may differ slightly from that of the aqueous salt solution used to prepare the emulsion. Generally speaking, however, an invert emulsion drilling fluid wherein the aqueous phase is saturated with sodium chloride may be used where the vapor pressure of the formation has a value (P) about three-fourths of the vapor pressure of water (P_w) at the same temperature (i.e., a relative vapor pressure of 0.75). Referring to FIG. 8, such a mud would be successful in drilling the deep, hard, West Texas shale (A) shown there which possesses a natural water content of about 2.2 weight percent. In that regard, it should be noted that hard argillaceous shales seldom exhibit relative aqueous vapor pressures in excess of 0.75. The deep, hard, Louisiana shale (B), for example, would normally be drilled with an invert emulsion fluid wherein the aqueous phase consists of saturated calcium chloride solution (i.e., a relative vapor pressure of 0.30). This shale has a connate or natural water content of about 1.8 or 1.9 weight percent. The soft, gumbo shale (C) has a connate or natural water content of about 11 weight percent and is best satisfied by a fluid with an aqueous phase vapor pressure less than a saturated aqueous NaCl solution.

C. Emulsion Drilling Fluids Designed by the Methods of the Invention.

Referring specifically to water-in-oil invert emulsion drilling fluids, a variety of such fluids are commercially available for use in drilling wells. Fluids of this type may be modified by the addition of vapor pressure depressants and can be used for drilling through water-sensitive formations difficult to drill with the commercial fluids. Typical invert emulsion drilling fluids contain droplets of water finely dispersed or emulsified in an oil base. Diesel fuels, kerosenes, and high-gravity crude oils are frequently used as the oil base, and about 10 to 70 percent of fresh or common salt water is emulsified therein with the help of suitable emulsifying and stabilizing agents. Anionic, nonionic, and mixed anionic-nonionic emulsifiers are all used for this purpose. The emulsifiers and stabilizing agents employed in the fluids should be compatible with sodium chloride, calcium chloride, or whatever water vapor pressure depressant is to be incorporated in the aqueous phase of the modified compositions. One specific invert emulsion drilling fluid composition which has been tested and appears satisfactory for many applications comprises 70 volume percent No. 2 diesel fuel, 23 volume percent water saturated with calcium chloride, and 5 volume percent sorbitan mono-oleate as the emulsifier. No difficulty, however, has been encountered in obtaining other satisfactory compositions simply by adding sodium chloride or calcium chloride to certain existing commercially available invert emulsion drilling fluids. Where formations are particularly water-sensitive it may be desirable to prepare a drilling fluid having a vapor pressure which is less than that of a mud containing a saturated calcium chloride solution. Solutions containing $ZnBr_2$, $ZnCl_2$, $LiBr$, $LiCl$, or similar water-soluble salts can be employed for this purpose. In addition, it has been found that a supersaturated $CaCl_2$ mud can be formed by adding additional $CaCl_2$ to a mud having a saturated $CaCl_2$ solution as the aqueous phase. Such supersaturated $CaCl_2$ muds have vapor pressures lower than those of saturated $CaCl_2$ muds. Other water vapor depressants contemplated to be useful in the various embodiments of this invention include still other water-soluble salts; phosphoric acid, acetic acid, and other water-soluble acids; glycerol, sodium hydroxide; potassium hydroxide; etc.

D. Monitoring the Drilling Fluid at the Wellsite

Once a compatible drilling fluid has been selected and introduced into the drilling system, it is advisable to monitor the fluid periodically to insure retention of compatibility. Contaminants, absorption, and other phenomena may cause gradual changes in the composition of the mud. Monitoring

can be rapidly accomplished by periodically immersing samples of successive formations penetrated by the well in portions of the mud in contact with these formations and logging the direction and extent of water migration between each such sample and the mud in which it is immersed with the displacement transducer apparatus.

In some cases it may be desirable to monitor the mud with calibrated shale samples having known vapor pressures. These calibrated samples may be preserved samples of the formation being drilled that have been taken from another well. Synthetic shale specimens, clay specimens, and the like, prepared so that they have particular aqueous vapor pressures can also be used. Calibrated shale samples representative of the water-sensitive formation are equivalent to substantially unaltered formation samples and the necessity for obtaining such samples from the well being drilled can thus be eliminated. By comparing an oil-base fluid of unknown aqueous vapor pressure with shale samples having known aqueous vapor pressures, it is apparent that the vapor pressure of the fluid can be determined. In this connection, it may be desirable to continuously monitor the aqueous vapor pressure of the oil-base mud with the displacement transducer and compare it with the formation vapor pressure. Another convenient method to monitor the aqueous vapor pressure of the mud is to place a sample in a closed container and directly measure the relative humidity of the atmosphere in contact with the samples as discussed above.

The condition and composition of the oil-base fluid can be determined by periodically emulsion-breaking a mud sample and determining its water content. In addition, the water can be analyzed for its content of vapor pressure depressant. Thus, if the vapor pressure of the aqueous phase is being controlled by the presence of calcium chloride, the aqueous phase can be analyzed for this salt.

The condition of the drilling fluid can also be qualitatively evaluated by observing the cuttings produced in the drilling operation if the water-sensitive formation is such that it will undergo visible deformation as it absorbs water. If the cuttings are firm and uniform, it can therefore be inferred that the fluid and the formation are in satisfactory condition. On the other hand, if the cuttings become softer or more diffuse, the concentration of the vapor pressure depressant in the aqueous phase of the fluid should be increased.

If an invert emulsion drilling fluid prepared in accordance with the invention loses water from its aqueous phase during drilling, it is probable that the water is being absorbed by the surrounding formation, and if this is the case, drilling conditions will tend to become more adverse. It is therefore desirable, under such circumstances, to add vapor pressure depressant to the aqueous phase of the fluid until its aqueous vapor pressure is no greater than the aqueous vapor pressure of the formation being drilled. This can generally be done by vigorously mixing the fluid at the surface of the earth with fresh depressant.

As noted previously, drilling fluids prepared in accordance with the present invention are especially applicable for use in the drilling of hard shales. Until the advent of this invention, there has been no satisfactory procedure for dealing with such shales. As noted previously, such hard shales generally have aqueous activities less than 0.75 which corresponds to a saturated solution of NaCl. The results obtained in accordance with the invention have shown that invert emulsion fluids wherein the aqueous phase is water saturated with calcium chloride are remarkably effective for a wide variety of such shales. If, during the course of drilling such a shale, additional calcium chloride must be added to the mud system, this may be done by mixing powdered calcium chloride into the fluid. Powdered calcium chloride has been found to readily enter the aqueous phase of an invert emulsion drilling fluid.

Abnormal pressure zones represent serious drilling hazards in many areas where wells are drilled. One characteristic of such zones is a transition zone that lies just above the abnormal pressure zone and that exhibits a marked increase in water

content. Since a corresponding increase may also be observed in the water activity of shales in the transition zone, continuously logging the activity of formations penetrated provides a method of detecting abnormal pressure zones. Water activity of a shale is reflected by the ratio of its aqueous vapor pressure to the vapor pressure of pure water at the same temperature, i.e., relative humidity. It may therefore be desirable to log the aqueous vapor pressure of the drill cuttings of the formations as they are penetrated. Measurements can be performed by exposing the cuttings to atmospheres of varying known humidities as discussed above, by placing the cuttings in a closed container and directly measuring the relative humidity of the atmosphere in contact with them as also discussed above, or by using the displacement transducer apparatus in conjunction with a series of oil-base fluids having known aqueous vapor pressures. If the aqueous vapor pressure of the shale is equal to that of the oil-base fluid, when the shale sample is placed in contact with the fluid it will exhibit no deformation.

II Use of the Methods of the Invention for Other Fluids

A. Treating Fluids

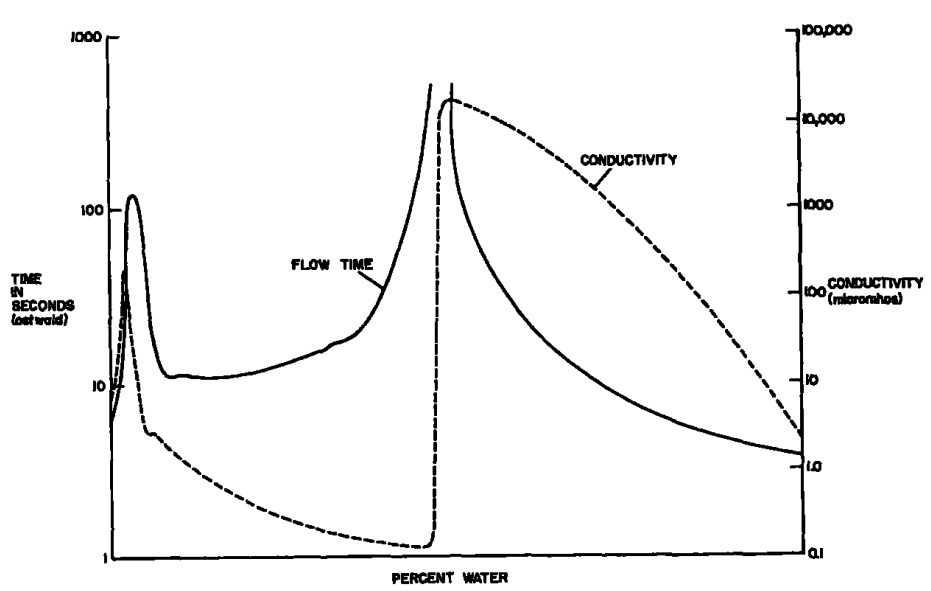
The principles of this invention are also applicable to other-wise conventional well fluid compositions such as packer fluids, coring fluids, completion fluids, and well treating fluids. With respect to treating fluids, for example, the methods and apparatus of the invention are useful in designing fluids for repairing and restoring water-damaged formations. In the past, it has been conventional practice in the field to attempt to restore water-damaged formations by treating them with concentrated salt water (30,000-50,000 ppm) or with solvents such as alcohols which have at least some degree of miscibility with both water and hydrocarbons. In accordance with the present invention, a suitable treating fluid is a water-in-oil emulsion wherein the aqueous phase has a sufficiently low vapor pressure so as to attract water from the damaged formation, thereby dehydrating and restoring the formation. Suitable oils for use in the emulsion include diesel fuels, kerosenes, light fuel oils, light crude oils, light petroleum fractions, LPG's, and the like. Oil-base and water-in-oil invert emulsion drilling fluids containing vapor pressure depressants are also generally suitable for use as packer fluids, coring fluids, completion fluids, etc.

B. Displacement Fluids

The principles of the invention are also applicable to fluid compositions and methods used in displacing oil from reservoirs. In recent years, for example, it has been observed that water-in-oil emulsions and microemulsions are useful in displacing oil from reservoirs. Such fluids generally are prepared from the same types of oils used to prepare invert emulsion treating fluids. Soluble oils have been employed to form microemulsion displacement fluids. Such formulations are typified by the displacement fluids disclosed in U.S. Pat. No. 3,254,714. The emulsion or microemulsion is injected into a reservoir at one point and driven from that point through the reservoir toward a second point where displaced oil is recovered from the reservoir. Since such emulsions and microemulsions have a substantial degree of miscibility with reservoir oils, and since their viscosities can be controlled to a considerable degree, they appear attractive for use as oil-displacing media. If such fluids, however, are employed in formations which are shaley or have shale streaks, there is a tendency for the shales to interfere with the effectiveness and stability of the emulsions. This tendency can be reduced through application of the present invention by controlling the vapor pressure of the aqueous phase of the emulsions or microemulsions so that it is substantially equal to or less than the aqueous vapor pressure of the shaley constituents of the formation. The manner of control is the same as that described for drilling fluids earlier in this disclosure. Since the vapor pressure of droplets of a liquid become significantly higher than the vapor pressure of the bulk liquid itself if the droplets are small enough, droplet diameter can be a design consideration in formulating microemulsion displacement fluids. Data on the effect of droplet diameter is presented by Paul Becher on

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June 7, 1966 W. B. GOGARTY ET AL 3,254,714
USE OF MICROEMULSIONS IN MISCIBLE-TYPE OIL RECOVERY PROCEDURE
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3,254,714

USE OF MICROEMULSIONS IN MISCIBLE-TYPE OIL RECOVERY PROCEDURE

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10 Claims. (Cl. 166-9)

This application is a continuation-in part of our co-pending United States patent application Serial No. 212,134, filed July 24, 1962, and Serial No. 324,216, filed November 18, 1963

This invention relates to the use of improved flooding materials in secondary-type oil recovery operations. More particularly, it relates to the use of microemulsions in such oil recovery operations

United States Patents 3,082,822 and 3,126,952 teach the use of solutions of surfactants in hydrocarbons in secondary oil recovery. Caszar, United States Patent 3,163,214 teaches the use of substantially anhydrous soluble oils in secondary-type oil recovery. Nominal amounts of water are contained in some of the systems described in this patent. This solution of this last patent are diluted with inert nonaqueous solvents to obtain desired viscosities.

Caszar uses general terms in describing a number of the components of his solutions. Stable systems which were formulated in an attempt to approximate the systems described by this patent reveal that the further addition of water increases their viscosity. This viscosity behavior is also common to the anhydrous "stock" systems to which water was added to formulate the water-containing "soluble oils" described in applicants' Serial No. 212,134 and Serial No. 324,216 and used in completed field tests.

We have discovered that water can be readily substituted for the nonaqueous solvent utilized in the Caszar patent under certain limited conditions and that the resulting "soluble oils" can be used in secondary and tertiary oil recovery.

This invention is based on the discovery that the phenomena described in the following paragraphs are common to substantially "anhydrous soluble oils" on addition of water. "Anhydrous soluble oils" are defined as quite stable, substantially clear, solutions of surfactants in nonpolar solvents where the surfactant concentration, including the concentration of cosurfactants, is substantially above the critical micelle concentration in the nonpolar solvent. This phenomenon may also be applicable to the liquid crystal system where the surfactant concentration is quite high. When water is incrementally added to the anhydrous soluble oils, assuming a chemical balance (approached by the hydrophile-lyophile balance or other methods) is reached and that the anhydrous soluble oil is compatible with the water, a series of phenomena have been found to occur. The phenomena occurring on initial addition of water will be discussed below in the order of their occurrence.

First region of water content.—The micellar system is stable and substantially clear. The viscosity has been found to rise in every instance tested on the incremental addition of water to the system.

Second region of water content.—The system is turbid and quite stable. There is usually a continued increase in viscosity on addition of water.

Third region of water content.—The system is turbid. The system apparently increases in instability with increasing water content. Generally, the viscosity decreases or levels off.

Fourth region of water content.—The systems of this water content are clear and stable. The viscosity of

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these systems is often relatively low when compared to the high viscosities found at the wet side of the second region of water content and the drier side of the third region of water content.

Continued water addition usually results in other phenomena and a sometimes irregular trend of viscosity with a final increase to a peak associated with an inversion of the system to an oil-in-water opaque or opalescent emulsion. Sometimes there is instability and inversion prior to the occurrence of the large viscosity peak associated with inversion. This latter phenomenon has been noted in systems utilizing light hydrocarbons, such as butane, as the nonpolar external phase.

It is postulated that turbidity occurs in the oil-external systems during water addition as the micellar systems are changing from one or more forms of micelle stable at lower water concentrations to one or more forms stable at higher water concentrations. It should be noted that turbidity and opacity occur when the dispersed phase has a refractive index differing from that of the external phase. Generally, these phenomena would not be seen where the refractive indices were the same. The water concentrations at which the postulated micellar forms change vary with surfactant concentration, the number and type of surfactants, water concentrations, temperatures, salt concentration, etc.

The first viscosity peak normally occurs between about 2 and 15% water concentration while the peak associated with inversion occurs at water concentrations ranging from lower than about 15% to higher than about 40% water.

Differences in the first and second regions of water content and later regions of water content are pointed up by the following phenomena which were found in all systems tested:

(1) The electrical conductivity of the systems on the dry side of this first peak increase to a maximum at a water concentration slightly lower than that causing the viscosity peak and then decreases to a minimum and then rapidly increases at about the water concentration needed to invert the oil-external system to a water-external system. This phenomenon is depicted by the stylized dashed line of the drawing.

(2) Treatment of fluids of region 2 with ultrasonic energy reduces the viscosity of these systems markedly. However, on completion of the treatment, the viscosity rapidly rises to approximately its former level. Conversely, as much as a week is required for the systems of region 3 to regain substantially their initial viscosity after ultrasonic irradiation.

(3) While the ultrasonic wave-induced low viscosity exists, the depressed viscosity system of region 3 will take up water more readily than will the depressed viscosity system on the dry side of the peak.

The fluids utilized in the process of this invention contain an amount of water sufficient to form systems having a nonpolar external (continuous) phase and the properties of the third or higher regions of water content as delineated above. These systems are hereinafter termed "water-containing soluble oils" to differentiate them from the substantially anhydrous soluble oils of the art. Preferably, the fluids utilized in the process of this invention contain at least that amount of water necessary to formulate the systems described under the heading "Fourth Region of Water Content." Generally, these systems are clear but may be turbid—i.e., hazy or cloudy—prior to the opacity occurring on the inversion of these systems through addition of additional water. These preferred systems are referred to hereafter as "microemulsions."

It is apparent that many different components may be utilized in the manufacture of compositions useful in this invention. Further, new surfactants, cosurfactants, etc.,

are constantly being developed and made commercially available. Many of these components will undoubtedly be found to be adaptable for the preparation of "water-containing soluble oils" and "microemulsions" useful in the present invention. It should be equally obvious that the properties of these systems will vary from those described above. The invention claimed lies in the use of water as an inexpensive diluent rather than the relatively expensive hydrocarbon diluents used in the prior art. To formulate a "water-containing soluble oil" or "microemulsion" useful in applicants' process will call for chemical knowledge and skill, but the duty of the colloid chemist will be like that of an architect who prescribes in the construction of a building the proper materials and the proper dimensions therefor. From his knowledge as a chemist of the materials available, the routine procedures available in this field, and the requisites for such a process, he will know or deduce with confidence their applicability in the preparations of fluids useful in the invention or, otherwise, in the case of novel materials he will know routine tests which will provide reliable data. While it is acknowledged that chemists, using the skill of the art, can formulate systems of sufficient instability or costs to preclude their use in commercial field operations, we may safely assume that no one will wish to make such a useless composition or will be misled because it is possible to misapply the teachings of this specification in order to do so.

Applicants' invention comprises injecting into a subterranean oil-bearing formation, through at least one injection well drilled therein, relatively stable substantially transparent "water-containing soluble oils" driving the said soluble oils toward at least one production well drilled into said oil-bearing formation, and recovering petroleum fluids through at least one production well.

The invention is illustrated by further reference to the drawing which also depicts, in stylized form, viscosity behavior observed on the addition of water to stable Czeaszar-type solutions or applicants previously mentioned anhydrous "stock" solutions. It is not intended that this drawing be representative of viscosity behavior for all useful "water-containing soluble oils" as these curves vary with component concentration, surfactant surfactant concentration, etc. It is seen that, on addition of small amounts of water, the viscosity increases to a first viscosity peak. On addition of still more water, the viscosity decreases. The decrease often ends in a small viscosity peak such as that shown at about 10% water concentration. One or more of such small peaks can be observed on the addition of water to the "soluble oils" found, as depicted between about 10% and about 33% water concentration. When sufficient water is added, at about 33%—as depicted, this system becomes slightly turbid and finally the viscosity increases to the inversion point at about 50% water concentration.

Microemulsions are made up of a nonpolar external or continuous phase which is preferably a hydrocarbon, a polar internal or discontinuous phase which is preferably water, and at least one surfactant. One or more cosurfactants or cosolvents (cosolubilizers) can also be utilized. "Water-containing soluble oils" and "microemulsions" are, for purposes of this invention, relatively stable and relatively transparent water-in-oil dispersions. Microemulsions have been called "transparent emulsions." One description of some microemulsions is found in Schulman and Montagne, *Annals of the New York Academy of Sciences*, 92, 366-71 (1960). The microemulsions, obviously, will not be transparent if made up of certain crude oils or other components which contain various color bodies as impurities.

The microemulsions used in this process are mobile and stable to the ions and fluids in the formation, i.e. they do not break readily in the presence of these materials. These microemulsions can contain additives to insure optimum operations, for example, corrosion in-

hibitors can be used in sour fields and bactericides where necessary.

Preferably, microemulsions used in the process of this invention contain, by volume, from about 45 to about 85% hydrocarbons, from about 10 to greater than 40% water, at least about 5% surfactant, and a cosurfactant.

Materials which can be used as the petroleum-base constituents of useful microemulsions include petroleum crudes, for example, a sweet crude from the Illinois Basin, "light ends," kerosene, octane, and pentane.

Alcohols containing up to about 8 carbon atoms are preferred cosurfactants in the microemulsions of this invention. Ethanol, isopropanol, 2-pentanol, isobutanol, cyclo-hexanol, cresol, and phenol are preferred alcohols. The secondary lower aliphatic alcohols, particularly isopropanol, are the most preferred alcohols for use in the composition of the banks used in the process of this invention. Other solubilizing compounds (cosurfactants) such as lower molecular weight amines and ketones can also be used.

Surfactants which can be used include the various nonionic, cationic, and anionic surfactants. Examples of such surfactants include sodium glyceryl monolaurate sulfate, dihexyl sodium succinate, hexadecyl-naphthalene sulfonate, diethyleneglycol sulfate, glycerol disulfate, monomylristate, p-toluidene sulfate laurate, p-chloroaniline sulfate laurate, sodium sulfato oleyl-ethylamide, triethanolamine myristate, N-methyltaurine oleamide, pentaerythritol monostearate, polyglycerol monolaurate, triethanolamine oleate, morpholine stearate, hexadecyl trimethylammonium chloride, dodecyl-dimethyl ammonium chloride, n-dodecyl-diethyleneglycol sulfate, monobutylphenyl phenol sodium sulfate, and triethanolamine laurate or triethanolamine oleate.

We prefer to utilize anionic surfactants such as higher alkylaryl monosulfonates, particularly alkyl-naphthenic monosulfonates, wherein the alkyl radical contains from about 10 to 20 carbon atoms. The sodium salts of dialkylsuccinates are also particularly desirable surfactants for use in making up the microemulsions. It is preferred that the alkyl radicals of the succinate compounds contain from about 6 to about 10 carbon atoms.

Microemulsions utilizing chlorinated solvents as the nonpolar phase are preferentially prepared utilizing a nonionic surfactant such as the sodium sulfate derivative of 3,9-diethylundecanol-6 or the sodium sulfate derivative of 7-ethyl-2-methylundecanol-4. Amine detergents, for example, 1-hydroxyethyl-2-heptadecenyl glyoxalidine, are preferred where the water in the formation is acidic or contains relatively large amounts of calcium or heavy metal ions.

The type of microemulsion and surfactant utilized in the microemulsion depends upon the temperature of the formation and the hardness, including salinity, and pH of the connate water and the water used to make up the microemulsion. It would be futile to use a detergent such as sodium oleate in a formation containing relatively high concentrations of calcium and magnesium ions, as the precipitated calcium and magnesium soaps would plug the formation. Where there is a natural detergent in the crude, a surfactant having a similar ionic charge must be used to avoid precipitating an insoluble reaction product. Preferably, the microemulsion can emulsify large amounts of fresh water and has a low viscosity at the point where the microemulsion inverts to form a water-external emulsion.

Water is the preferred polar solvent and is preferably soft. However, ordinary hard tap water and even relatively brackish waters can be used with detergents which are stable to the contaminating ions. The water utilized can be of a class designed to overcome problems arising out of the water sensitivity of a particular formation. Techniques used in preparing microemulsions are known. The composition is generally prepared by dissolving the surfactant in the nonpolar constituent. However, the

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surfactant can also be included in the polar constituent. Preferably, the surfactant and cosurfactant are dissolved in a petroleum fluid, and water is added to the petroleum fraction incrementally with agitation.

The amount of slug used increases, though the percent of pore volume decreases, with the volume of reservoir to be swept. Thus, 2.5 to 5.0% of pore volume are adequate to flood a 40-50-acre area, while 5-10% of pore volume are necessary for a 5-10-acre area.

We prefer to inject into the formation a slug of microemulsion bank material of from 1-20% and at least about 3 to about 10% of the pore volume of the formation. Thirty percent, or more, bank material can be utilized. However, such large banks can prove economically unattractive.

It is difficult to define the exact amount of bank material required in this process. Ideally, sufficient bank material should be used to provide a substantially continuous zone of bank material, at the perimeter of the area from which it is desired to recover petroleum crude, between the crude in the formation and the material used to drive the bank. Sometimes it may be more economical to use a small slug, expecting substantial breaks in the bank at the final perimeter, to obtain only a partial recovery of crude rather than to use a large slug and obtain a complete recovery in the swept area. The amount of bank required will also vary with the area to be swept. Crude viscosity, substantial variations in formation permeability, and other considerations also affect the pore volume to be used. Thus, increased amounts of bank material are required where the viscosity of the crude is high in order that the incremental drops in viscosity from the high viscosity at the leading edge to the low viscosity at the trailing edge will be small.

After injection of the bank is completed, a drive mate-

ing $C_{12}H_{25-30}SO_3Na$, with $n=25-30$ and having a long paraffinic chain attached to an aromatic-naphthenic nucleus, is mixed with the gasoline. The water is then dumped into the container and thereafter rapidly agitated at temperatures of about 30-34° C. Higher temperatures cause some cloudiness and high viscosities. Thus, 400 ml of a mixture containing 7.4% sulfonate, 49.6% straight run gasoline, and 43% water require about 30 minutes to become transparent with vigorous agitation.

EXAMPLE II

Four floods are performed in an unconsolidated sand packed (Blackhawk B Sand) into 10' x 0.5" pipe. The pack has a porosity of 37.7% and a permeability of 10 d. In each test, the sand pack is prepared in the same manner with Illinois water. Hughes crude is injected into the sand pack as the oil phase, and air is injected as the gas phase. The various slugs are followed by fresh water at a constant injection rate of 36.7 cc/hr.

Various floods and slugs are utilized in a series of experiments set out in the table below. A slug is made up of 24% water, 3.8% isopropanol, 11.6% alkylaryl naphthenic sulfonate, and 60.6% straight run gasoline. The slug should have a viscosity of about 11 cp. A 40% water content, nonalcoholic microemulsion is made up of 40% water, 44% straight run gasoline, and 16% sulfonate. The nonalcoholic microemulsion should have a viscosity of about 15 cp. An emulsion containing 60% water, 2% isopropanol, and 38% of a straight run gasoline-alkylnaphthenic sulfonate mixture in a ratio of 84:16. The emulsion should have a viscosity of about 11 cp.

Comparable results are obtained with the nonalcoholic transparent emulsion only when the slug is tapered with a second slug of 12% pore volume of a water external, 60% emulsion containing alcohol.

Displacement efficiencies of alcoholic and nonalcoholic systems

Pore Volumes to be Injected	Straight Slug 12% PV 24% H ₂ O (alcoholic)	Straight Slug 12% PV 40% H ₂ O (nonalcoholic)	Tapered Slug 12% PV 8% of 40% H ₂ O 6% of 60% H ₂ O	Tapered Slug 24% PV 12% of 40% H ₂ O 12% of 60% H ₂ O
Miscible Slug Secondary Oil Recovery--Percent of Original Oil in Place				
1/4	24.4	25.8	27.8	28.0
1/2	28.8	28.8	28.4	28.7
1 1/4	28.4	28.7	28.3	28.3
Initial Fluid Saturations--Percent of Pore Volume				
Water Sat.	18.1	14.2	14.2	18.1
Oil Sat.	67.8	68.4	67.8	66.6
Air Sat.	14.1	17.4	18.0	15.3

rial is injected into the formation, usually through the same injection wells, to force the bank material through the formation and the crude ahead of the bank material. Water or thickened water is the preferred drive material. Other drive materials are also useful. Examples of such materials include nitrogen, carbon dioxide, and natural gas.

The following specific examples more fully illustrate our invention, but it is not intended that our invention be limited to the exact petroleum constituents, surfactants, cosolvents, or procedures utilized. Rather, it is intended that all equivalents obvious to those skilled in the art be included within the scope of our invention as claimed.

EXAMPLE I

Microemulsions, as defined above, are prepared from an alkylaryl sulfonate, water, and straight run gasoline. The sulfonate, having an empirical formula approximat-

EXAMPLE III

A pentane slug containing 3.4% isopropanol, 33% water, 51.0% pentane, and 12.6% commercial alkyl-naphthenic monosulfonate can be found to yield the following results when compared with a regular water flood in a sand pack such as that of Example II. Water is the drive material.

Secondary oil recovery percent of original oil in place (with 33% water content microemulsion)

Pore Volumes to be Injected	20% PV Slug Size	12% PV Slug Size	6% PV Slug Size	Regular Waterflood
1/4	28.4	27.7	21.0	- - -
1	28.0	28.2	21.7	27.0

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EXAMPLE IV

A pentane slug containing 16% isopropanol, 68% water, 24.5% pentane, and 6.1% alkyl-naphthenic mono-sulfonate gives the following recovery efficiency when tested in the unconsolidated sand pack of Examples II and III. Again, water is the drive material.

Secondary oil recovery percent of original oil in place (with 68% water-external emulsion)

Pore Volumes to be Injected	36% PV Slug Size	15% PV Slug Size
1	20.4 85.1	18.3 64.3

Now having described our invention, what we claim is:
1 In a process for the recovery of crude petroleum fluids from permeable subterranean formations having at least one injection means and one recovery means in fluid communication with said subterranean formation, the steps comprising injecting through at least one injection means a water-containing soluble oil, displacing said water-containing soluble oil toward at least one recovery means, and recovering substantial displaced crude petroleum fluids through said at least one recovery means.

2 The process of claim 1 wherein the water containing soluble oil is a microemulsion.

3 The process of claim 2 wherein the microemulsion contains from about 10 to about 20% water as a dispersed phase.

4 The process of claim 2 wherein the volume of microemulsion injected into the formation comprises from about 1 to about 20% of the pore volume of the formation being flooded.

5 The process of claim 2 wherein the volume of microemulsion injected into the formation comprises at least about 3 to about 10% of the pore volume being flooded.

6 The process of claim 2 wherein the microemulsion contains an at least partially oil-soluble sulfonate surfactant.

7 The process comprising injecting into a permeable crude oil-containing subterranean formation having at least one injection well and at least one recovery well in communication therewith, the process comprising injecting into said formation through said at least one injection well a microemulsion containing at least about 10% water as the dispersed phase, thereafter injecting into said formation through said injection well water to displace said microemulsion toward at least one recovery well and recovering substantial displaced crude petroleum fluids through said at least one recovery well.

8 The process of claim 7 wherein the volume of microemulsion injected into the formation comprises from about 1 to about 20% of the pore volume of the formation being flooded.

9 The process of claim 7 wherein the volume of microemulsion injected into the formation comprises at least about 3 to about 10% of the pore volume being flooded.

10 The process of claim 7 wherein the microemulsion contains an at least partially oil-soluble sulfonate surfactant.

References Cited by the Examiner

UNITED STATES PATENTS

3,163,214 12/1964 Csaszar ----- 166-9

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