



Industria y Comercio
SUPERINTENDENCIA

SOLICITUD
PATENTE DE INVENCION

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 11-107291- -00000-0000

Fecha: 2011-08-23 18:39:51 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eva: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 131

21. EXPEDIENTE No. _____

54. TÍTULO **"CONDUCCIÓN POR TUBERÍA DE PETRÓLEO
EN FORMA DE EMULSIÓN"**

51. CLASIFICACIÓN INTERNACIONAL **B01D 17/04**

71. SOLICITANTE **PACHECO, LUIS; BRICEÑO, MARIA Y
NUÑEZ, GUSTAVO, A.**

DOMICILIO **BOGOTÁ D.C., COLOMBIA Y CIUDAD DE
PANAMÁ, PANAMÁ**

74. REPRESENTANTE LEGAL **ALICIA LLOREDA RICAURTE**
T.P. 53.215

22. BOGOTÁ, D.C. _____

(FORMA P 10)

PETITORIO



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 11-107291-00000-0000

Fecha: 2011-08-23 16:39:51
Tra. 11 PATENTEIYII
Act. 411 PRESENTACION

Dep. 2020 DIR.NUEVASCR
Eve: 378 FASENACIONALI
Folios: 131

FORMULARIO ÚNICO DE SOLICITUD DE PATENTE PCT ENTRADA EN FASE NACIONAL

①

SOLICITUD DE:

☒ Patente de Invención

☐ Patente de Modelo de Utilidad

☒ Capítulo I.

☐ Capítulo II.

②

SOLICITANTE (71)

Nombre: **PACHECO, LUIS; BRICEÑO, MARIA Y NUÑEZ, GUSTAVO, A.**

Dirección: Carrera 14 No. 94-44, Torre A, Piso 6, Bogotá D.C., Colombia y City of Knowledge, Building 231, Clayton, Ciudad de Panamá, Panamá.

Nacionalidad o Domicilio: Bogotá D.C., Colombia y Ciudad de Panamá, Panamá.

Lugar de Constitución:

Teléfono: 3264270 Fax: 6069701

E-mail: jllcco@lloredacamacho.com

IDENTIFICACION

C.C. ☐ NIT ☐
C.E. ☐ Otro ☐

Cual _____

Número _____

③

REPRESENTANTE O APODERADO

Nombre: **ALICIA LLOREDA RICAURTE**

Dirección: Calle 72 No. 5-83 Piso 5º, Bogotá, Colombia

Teléfono: 3264270 Fax: 6069701

E-mail: jllcco@lloredacamacho.com

C.C. ☒ NIT ☐
C.E. ☐ Otro ☐

Cual _____

Número 39.690.713 TP 53.215

④

INVENTOR(ES) (72)

Nombre: **PACHECO, Luis; BRICEÑO, Maria y NUÑEZ, Gustavo, A.**

Dirección: Carrera 14 No. 94-44, Torre A, Piso 6, Bogotá D.C. y City of Knowledge, Building 231, Clayton, Ciudad de Panamá, Panamá.

Nacionalidad o Domicilio: Colombia y Panamá.

⑤

PCT (86)

Solicitud Internacional No. PCT/IB2010/000317

Fecha: 29/01/10

Publicación Internacional No. WO 2010/086742 A1

Fecha: 05/08/10

⑥

Título (54)

"CONDUCCIÓN POR TUBERÍA DE PETRÓLEO EN FORMA DE EMULSIÓN"

⑦

Clasificación Internacional (51) B01D 17/04

⑧

Prioridad

SI ☒ NO ☐

(33) País de Origen

US

(32) Fecha

29/01/09

(31) Número de Solicitud

61/148,306

⑨

Comprobante de Pago No. 11-0062699

Fecha: 28 de Junio de 2011

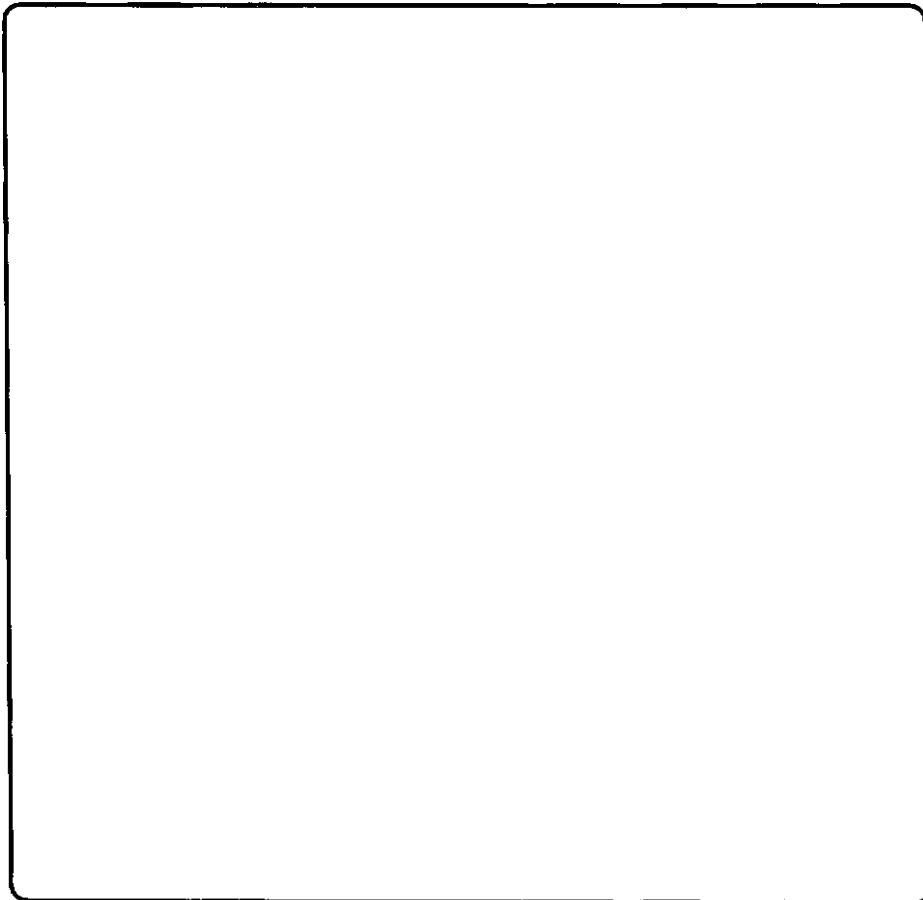
10

ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud.
- ☐ Documento que acredite la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☐ Documento de Representación Legal.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones.
- ☐ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☐ Copia del reporte preliminar internacional sobre patentabilidad.
- ☐ Traducción del reporte preliminar internacional sobre patentabilidad.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ Arte Final 12X12.
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionados parcial o totalmente con la invención de esta solicitud.
- ☐ De ser el caso, modificaciones efectuadas a la solicitud internacional.
- ☒ Otros: reporte de búsqueda internacional, anexos al reporte de búsqueda internacional, publicación y opinión escrita de la autoridad de búsqueda internacional.

11

FIGURA CARACTERISTICA:



12

Solicito la concesión de la patente,

NOMBRE: ALICIA LLORED A RICAURTE

FIRMA:

C.C. 39.690.713

T.P. 53.215

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
NIT : 800.176.089-2
- / -



RECIBO DE CAJA

No. 11 - 0062699

Bogotá D.C., Junio 28 de 2011 - 17:53:00

RECIBIDO DE : LLOREDA & CIA S.A.

NI 8.300.221.455

*** Soporte del Pago ***

TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	VR. PAGO
CONSIGNACION	BANCO DE BOGOTA	062754387	414999491	28/06/2011	21.073.000.00

*** Conceptos Pagados ***

CANT.	RENTISTICO	CONCEPTO	Vr. UNIDITARIO	Vr. CONCEPTO
1	50005-01-01 SOLICITUDES	110 PTC SOLICITUD DE PATENTE DE INVENCIÓN	571.000.00	571.000.00
				\$571.000.00

SON: **QUINIENTOS SETENTA Y UN MIL PESOS MONEDA CORRIENTE**

Responsable: 

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 11-107291- -00000-0000

Fecha: 2011-08-23 16:39:51 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 131

Sede Centro: Carrera 13 No. 27 - 00 Pisos 3,4,5 y 10 Bogotá, D.C.- Colombia

Web: www.sic.gov.co e-mail: Info@sic.gov.co Conmutador: (571) 5870000 Fax: (571) 5870284 Líneas: 018000-910165 Call Center: (571) 6513240

Junio 28 de 2011 - 17:53:06

 Industria y Comercio SUPERINTENDENCIA		SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO DIVISIÓN DE NUEVAS CREACIONES EXTRACTO PARA PUBLICACIÓN SOLICITUD DE PATENTE DE INVENCION PCT	
(21) N° de solicitud: (22) Fecha de solicitud: 23-08-11 (30) Prioridad (31) No. Prioridad 61/148,306 (32) Fecha 29-01-09 (33) País US		(51) Int Cl: B01D 17/04 (71) Solicitante(s): PACHECO, LUIS; BRICEÑO, MARIA Y NUÑEZ, GUSTAVO, A. (72) Inventor(es): PACHECO, Luis; BRICEÑO, Maria y NUÑEZ, Gustavo, A. (74) Apoderado: ALICIA LLOREDA RICAURTE	
(85) Fecha límite inicio fase nacional: 29-08-11 (86) Datos relativos a la presentación de la solicitud PCT Fecha de presentación de la solicitud: 29-01-10 No. de solicitud: PCT/IB2010/000317		(87) Publicación internacional Fecha: 05-08-10 N° publicación: WO 2010/086742 A1	
(54) Título: CONDUCCIÓN POR TUBERÍA DE PETRÓLEO EN FORMA DE EMULSIÓN			

Resumen - Reivindicación(es):

Sector: Industria Petrolera, en particular sistemas de conducción para productos viscosos que facilitan el transporte de líquidos viscosos por la modificación de la viscosidad, resultante de la mezcla con otro líquido, y procesos para romper emulsiones.

Resumen.-

Un medio para transportar una dispersión de petróleo crudo y agua mediante tuberías convencionales. La dispersión es una emulsión preparada mediante la combinación de agua de producción con petróleo crudo así como un sistema apropiado de tensoactivos de modo tal que la emulsión se estabiliza. La dispersión presenta una viscosidad de menos de aproximadamente 500 cP que permite que se pueda bombear y transportar vía tuberías convencionales. La dispersión, una vez llega a su destino final, se rompe o se separa mediante uno o más diluyentes apropiados de modo que el petróleo remanente cumpla con las especificaciones predeterminadas para procesamiento adicional, es decir, refinar en fracciones más ligeras.

		SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
Industria y Comercio		DIVISIÓN DE NUEVAS CREACIONES	
SUPERINTENDENCIA		TARJETA ARCHIVO PROPIETARIOS	
PATENTE DE INVENCION		PCT	☒ X
		MODELO DE UTILIDAD	☐
		DISEÑO INDUSTRIAL	☐
(21) N° de solicitud:		(22) Fecha de solicitud: 23-08-11	
(51) Clasificación Internacional: B01D 17/04			
(71) Solicitante(s): PACHECO, LUIS; BRICEÑO, MARIA Y NUÑEZ, GUSTAVO, A.			
(72) Inventor(es): PACHECO, Luis; BRICEÑO, Maria y NUÑEZ, Gustavo, A.			
(74) Apoderado: ALICIA LLOREDA RICAURTE			
(30) Prioridad	(31) No. Prioridad	(32) Fecha	(33) País
	61/148,306	29-01-09	US
(85) Fecha límite inicio fase nacional: 29-08-11		(87) Publicación internacional	
(86) Datos relativos a la presentación de la solicitud PCT		Fecha: 05-08-10	
Fecha de presentación de la solicitud: 29-01-10		N° publicación: WO 2010/086742 A1	
No. de solicitud: PCT/IB2010/000317			
(54) Título: CONDUCCIÓN POR TUBERÍA DE PETRÓLEO EN FORMA DE EMULSIÓN			

		SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
Industria y Comercio		DIVISIÓN DE NUEVAS CREACIONES	
SUPERINTENDENCIA		TARJETA ARCHIVO TEMÁTICO	
PATENTE DE INVENCION		PCT ☒ MODELO DE UTILIDAD	
DISEÑO INDUSTRIAL			
(21) N° de solicitud:		(22) Fecha de solicitud: 23-08-11	
(51) Clasificación Internacional: B01D 17/04			
(71) Solicitante(s): PACHECO, LUIS; BRICEÑO, MARIA Y NUÑEZ, GUSTAVO, A.			
(72) Inventor(es): PACHECO, Luis; BRICEÑO, Maria y NUÑEZ, Gustavo, A.			
(74) Apoderado: ALICIA LLOREDA RICAURTE			
(30) Prioridad	(31) No. Prioridad	(32) Fecha	(33) País
	61/148,306	29-01-09	US
(85) Fecha límite inicio fase nacional: 29-08-11		(87) Publicación internacional:	
(86) Datos relativos a la presentación de la solíc. PCT		Fecha: 05-08-10	
Fecha de presentación de la solicitud: 29-01-10		No. Publicación: WO 2010/086742 A1	
No. de solicitud: PCT/IB2010/000317			
(54) Título:			
CONDUCCIÓN POR TUBERÍA DE PETRÓLEO EN FORMA DE EMULSIÓN			
(57) Resumen:			
Sector: Industria Petrolera, en particular sistemas de conducción para productos viscosos que facilitan el transporte de líquidos viscosos por la modificación de la viscosidad, resultante de la mezcla con otro líquido, y procesos para romper emulsiones.			
Resumen.-			
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5

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 4200.04WO01	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/IB2010/000317	International filing date (day/month/year) 29/01/2010	(Earliest) Priority Date (day/month/year) 29/01/2009
Applicant PACHECO, LUIS		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the International search was carried out on the basis of:

- ☒ the International application in the language in which it was filed
☐ a translation of the International application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐ This international search report has been established taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rule 43.6b/s(a)).

c. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the International application, see Box No. I.

2. ☐ Certain claims were found unsearchable (See Box No. II)

3. ☐ Unity of invention is lacking (see Box No. III)

4. With regard to the title,

- ☒ the text is approved as submitted by the applicant
☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

- ☒ the text is approved as submitted by the applicant
☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the drawings,

a. the figure of the drawings to be published with the abstract is Figure No. 1

- ☒ as suggested by the applicant
☐ as selected by this Authority, because the applicant failed to suggest a figure
☐ as selected by this Authority, because this figure better characterizes the invention

b. ☐ none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2010/000317A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D17/04 B01F3/08 F17D1/17
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D B01F F17D C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 528 001 A (CANADIAN OCCIDENTAL PETROLEUM LTD) 1 February 1994 (1994-02-01) column 1, line 25 - line 37 column 17, line 5 - line 25; claim 1; examples XVIII, XIX column 41, line 59 - column 42, line 42 -----	1-20
X	EP 0 414 424 A2 (BRITISH PETROLEUM CO PLC [GB]) 27 February 1991 (1991-02-27) page 3, line 46 - line 47; claim 12 -----	1,3,6-9, 11-14,18
X	US 5 863 301 A (GROSSO JORGE LUIS [CO] ET AL) 26 January 1999 (1999-01-26) column 1, line 8 - line 14; claim 14; figure 6; example 3 ----- -/--	1-3,6-9, 11-14,18

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

29 April 2010

Date of mailing of the international search report

11/05/2010

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Redecker, Michael

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2010/000317

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 821 757 A (HAYES MICHAEL E [US] ET AL) 18 April 1989 (1989-04-18) column 44, line 24 - column 45, line 24 column 23, line 33 - line 57; claim 1 -----	1-3,6-9, 11-14,18
X	WO 81/02024 A1 (LANCO INC [US]) 23 July 1981 (1981-07-23) page 3, line 9 - line 19; claims 1,2,7,9,13 page 16, line 11 - line 24; examples 3,4 page 9, line 7 - line 14 -----	1,3,6-9, 11-13,18
X	US 5 354 504 A (RIVAS HERCILIO [VE] ET AL) 11 October 1994 (1994-10-11) column 1, line 8 - line 35; claim 1; example 1; table 2 -----	1-3,6-9, 11-13,18
A	US 5 480 583 A (RIVAS HERCILIO [VE] ET AL) 2 January 1996 (1996-01-02) the whole document -----	1-20
A	US 475 833 A (PFIZER INC) 19 July 1988 (1988-07-19) the whole document -----	1-20
A	US 5 641 433 A (CHIRINOS MARIA LUISA [VE] ET AL) 24 June 1997 (1997-06-24) the whole document -----	1-20

8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2010/000317

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 528001	A	NONE	
EP 0414424	A2	27-02-1991	BR 9004173 A 03-09-1991
		CA 2023465 A1 25-02-1991	
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US 5863301	A	26-01-1999	NONE
US 4821757	A	18-04-1989	NONE
WO 8102024	A1	23-07-1981	EP 0043843 A1 20-01-1982
US 5354504	A	11-10-1994	BE 1006034 A3 26-04-1994
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		IT 1256678 B 12-12-1995	
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		CA 2083803 A1 03-06-1993	
		DE 4240396 A1 03-06-1993	
		DK 141492 A 03-06-1993	
		ES 2048685 A1 16-03-1994	
		FR 2684897 A1 18-06-1993	
		GB 2262054 A 09-06-1993	
		IT 1257930 B 19-02-1996	
		NL 9202077 A 01-07-1993	
		NO 924514 A 03-06-1993	
		SE 505950 C2 27-10-1997	
		SE 9203534 A 03-06-1993	
		US 5503772 A 02-04-1996	
		US 5419852 A 30-05-1995	
US 475833	A	NONE	
US 5641433	A	24-06-1997	NONE

DOCUMENTOS ANEXOS AL REPORTE DE BÚSQUEDA INTERNACIONAL

- 1. US 528 001 A**
- 2. EP 0 414 424 A2**
- 3. US 5 863 301 A**
- 4. US 4 821 757 A**
- 5. WO 81/02024 A1**
- 6. US 5 354 504 A**
- 7. US 5 480 583 A**
- 8. US 475 833 A**
- 9. US 5 641 433 A**

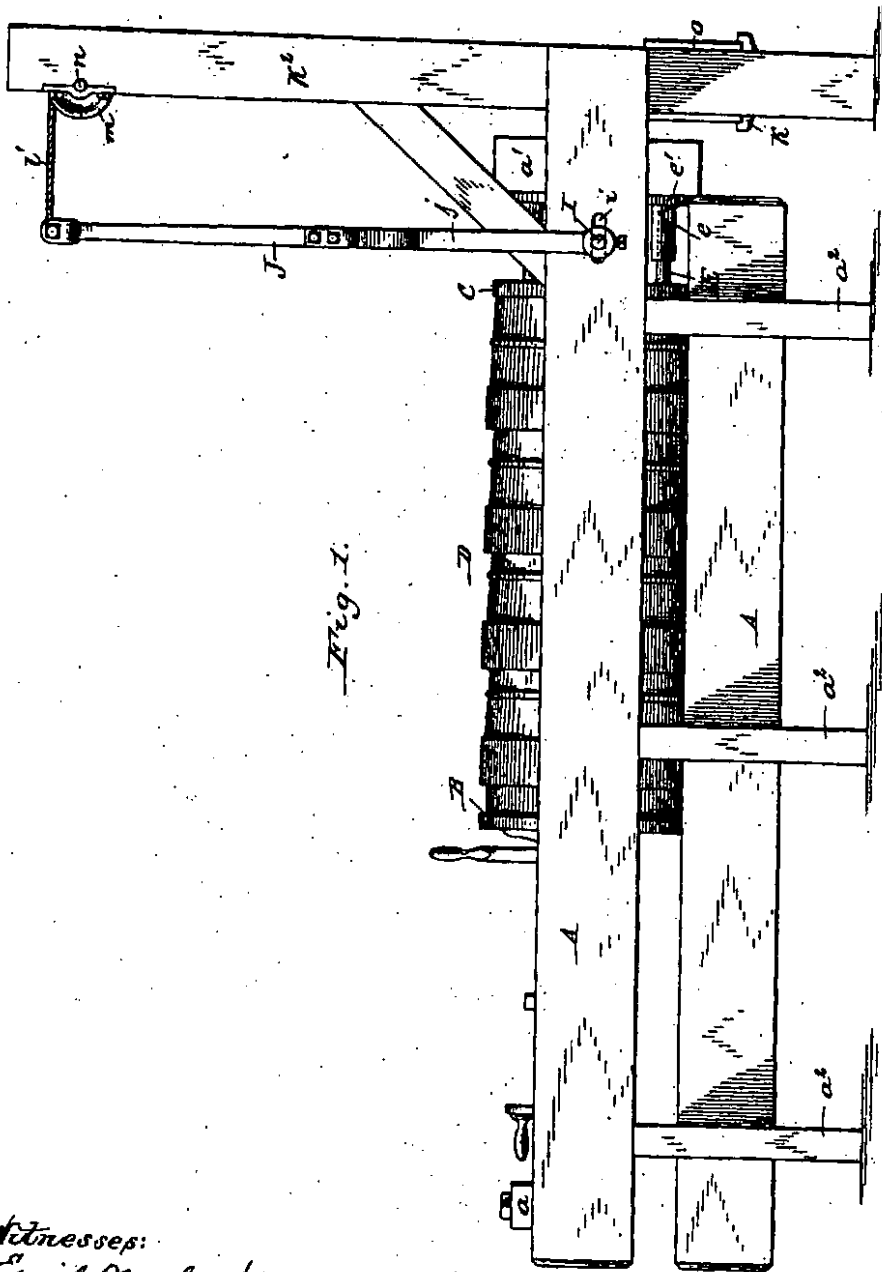
(No Model.)

C. J. LUNDSTROM.
CHEESE PRESS.

4 Sheets—Sheet 1.

No. 528,001.

Patented Oct. 23, 1894.



Witnesses:
Emil Newhart
Theo. L. Opp

Carl J. Lundstroms Inventor.
By Wilhelm A. Forner. Attorneys.

THE MONROE PETERS CO., PHOTO-LITHO., WASHINGTON, D. C.

(No Model.)

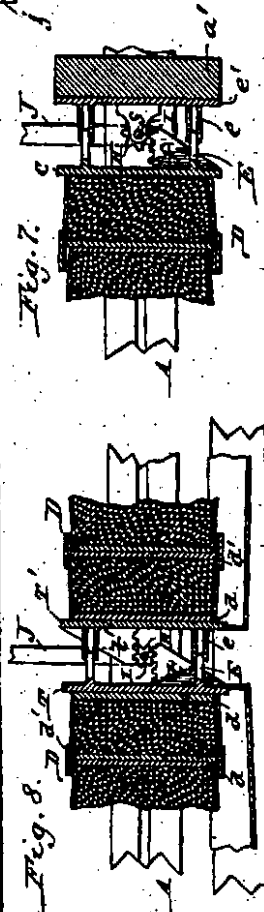
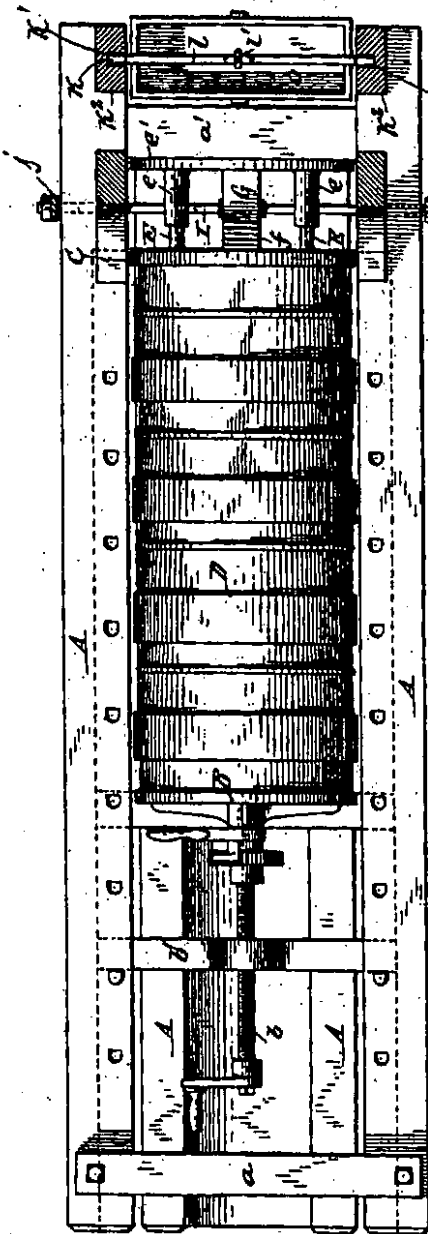
C. J. LUNDSTROM.
CHEESE PRESS.

4 Sheets—Sheet 2.

No. 528,001.

Patented Oct. 23, 1894.

Fig. 2.



Witnesses:

Emil Neuhart

Theo. L. Popp

Carl J. Lundstrom Inventor.

By Wilhelm Popp

Attorneys.

THE SCOTT PETERS CO. PHOTO-LITHO. WASHINGTON, D. C.

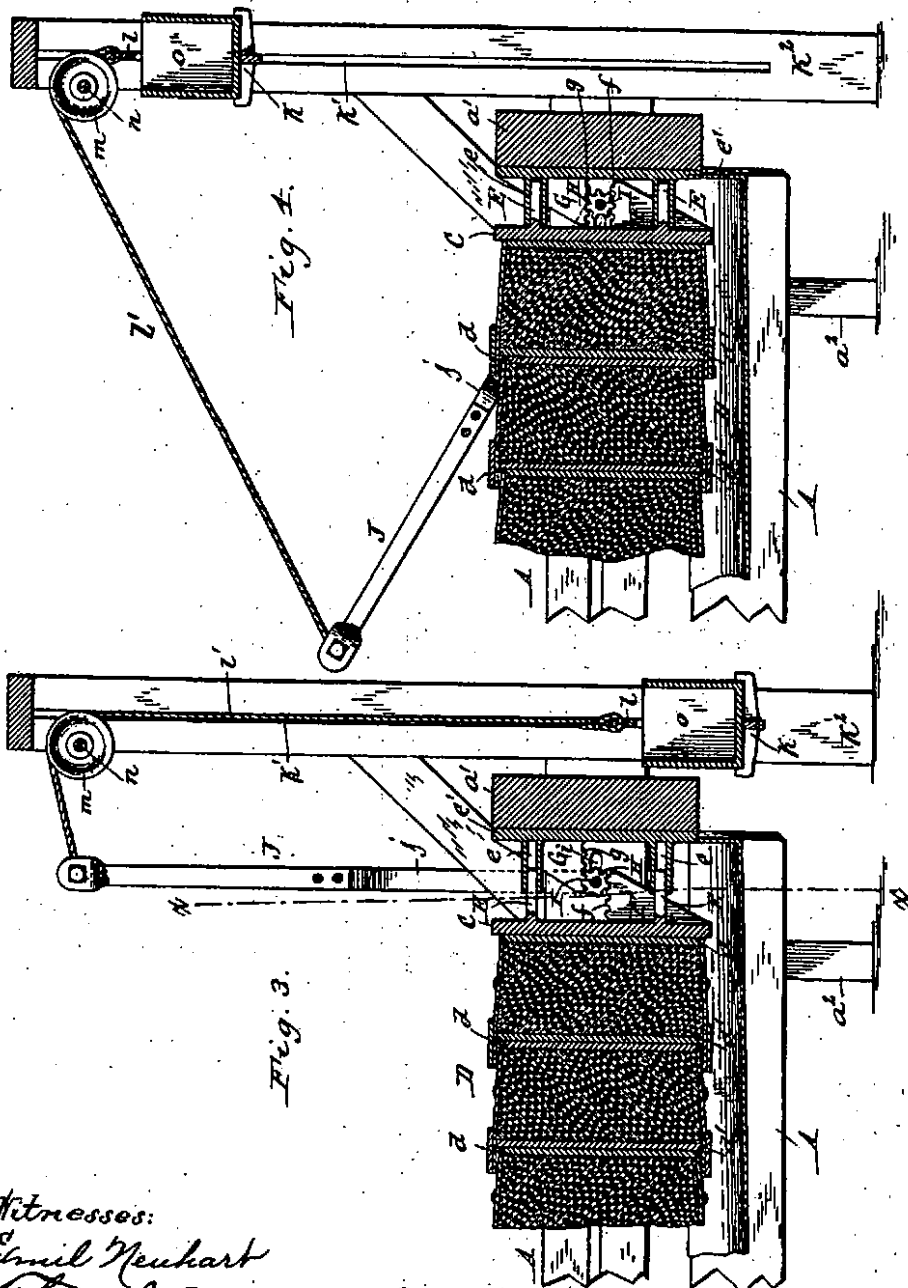
(No Model.)

C. J. LUNDSTROM.
CHEESE PRESS.

4 Sheets—Sheet 3.

No. 528,001.

Patented Oct. 23, 1894.



Witnesses:
Emil Neuhart
Theo. L. Popp.

Carl Lundstrom Inventor.
By Wilhelm Hornum Attorneys.

THE NORMAN BERRY CO., PHOTO-LITHO, WASHINGTON, D. C.

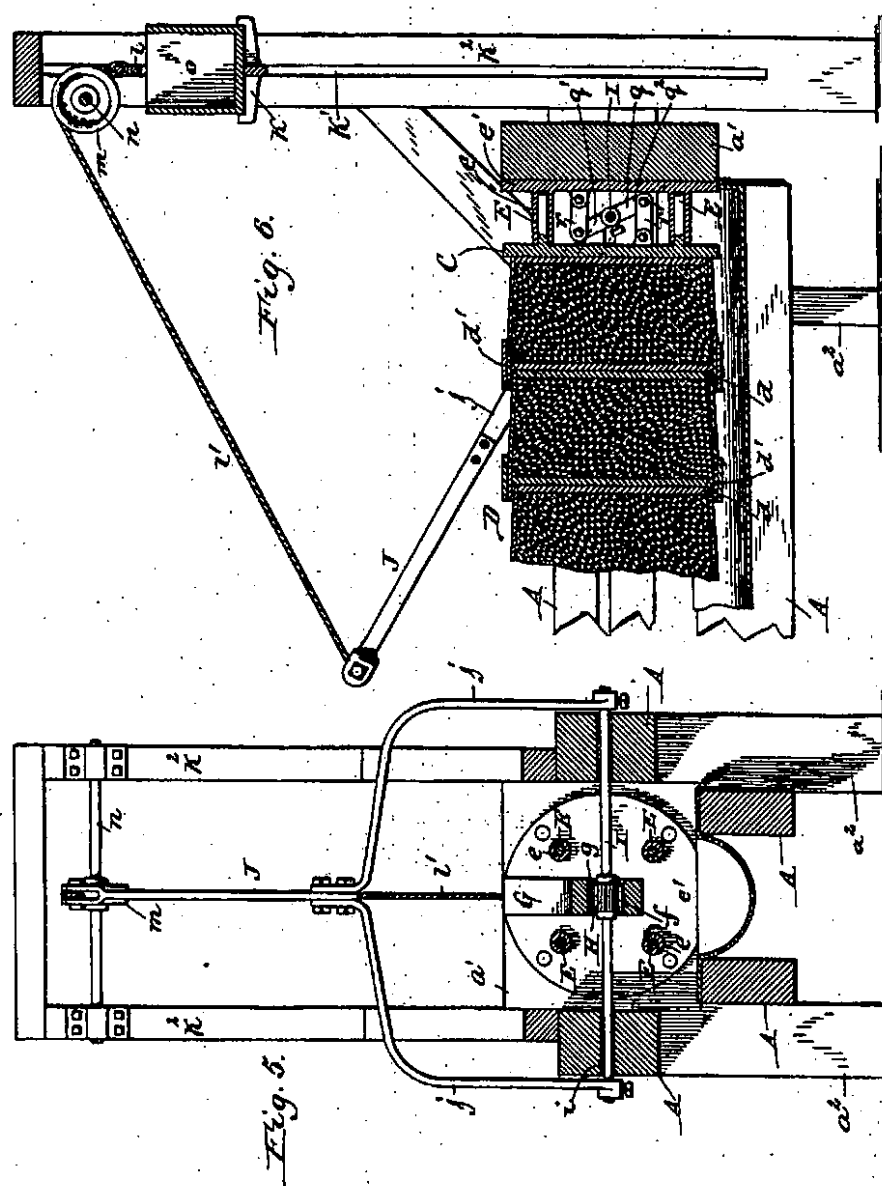
(No Model.)

C. J. LUNDSTROM.
CHEESE PRESS.

4 Sheets—Sheet 4.

No. 528,001.

Patented Oct. 23, 1894.



Witnesses:
Emil Neuhauf.
Thos. L. Popp.

Carl Sundstrom Inventor.
By William H. Bonded.
Attorneys.

THE HANSON ELECTRIC CO., BOSTON, LITHO. MANUFACTURED IN U.S.A.

UNITED STATES PATENT OFFICE.

CARL JOHAN LUNDSTROM, OF LITTLE FALLS, NEW YORK, ASSIGNOR TO
D. H. BURRELL & CO., OF SAME PLACE.

CHEESE-PRESS.

SPECIFICATION forming part of Letters Patent No. 528,001, dated October 23, 1894.

Application filed June 22, 1892. Serial No. 437,641. (No model.)

To all whom it may concern:

Be it known that I, CARL JOHAN LUNDSTROM, a subject of the King of Sweden and Norway, residing at Little Falls, in the county of Herkimer and State of New York, have invented new and useful Improvements in Cheese-Presses, of which the following is a specification.

This invention relates to that class of cheese presses in which the pressure is applied automatically. It is particularly designed for use in cheese presses in which the preliminary pressure is applied by hand and the final pressure is effected automatically, but it is also applicable to presses in which the pressure is applied automatically throughout the pressing operation.

My invention has the object to produce a simple, durable and efficient device whereby the pressure upon the cheeses is applied automatically.

In the accompanying drawings consisting of four sheets:—Figure 1 is a side elevation of a cheese press provided with my improvements. Fig. 2 is a top plan view thereof, partly in section. Fig. 3 is a longitudinal sectional elevation of the rear portion of the press, showing the position of the automatic pressure gear before applying the preliminary hand pressure. Fig. 4 is a similar view, showing the position of the final pressure gear after the preliminary pressure has been applied. Fig. 5 is a vertical transverse section in line $x-x$, Fig. 3. Fig. 6 is a longitudinal sectional elevation of the rear portion of a cheese press, showing a modified connection of the shaft of the weight lever with the foot block and press frame. Fig. 7 is a fragmentary longitudinal section, showing the shaft of the weight lever supported in fixed bearings on the press frame. Fig. 8 is a fragmentary longitudinal section, showing my improvements applied to a press in which two gangs of cheeses are pressed simultaneously. Like letters of reference refer to like parts in the several figures.

The press frame consists essentially of longitudinal side beams A, front and rear cross pieces a and supporting legs a' .

B represents the head block or follower which moves lengthwise between the beams.

b is the hand pressure screw whereby the head block is operated and which is arranged in a cross bar b' secured with its ends to the longitudinal beams.

C represents the longitudinally movable foot block arranged between the rear portions of the longitudinal beams.

D represents a gang of cheese hoops of any suitable construction placed between the head and foot blocks in the usual manner, each hoop having a perforated bottom d and a perforated cover or follower d' and bearing with its bottom against the follower of the next other, so that the hoops telescope into each other.

The foot block is guided in its horizontal movement by guide rods E which are formed on the rear side of the foot block and slide in stationary sleeves e formed on the front side of a supporting plate e' which latter is secured to the front side of the rear cross piece.

The rear side of the foot block is provided centrally with a rearwardly projecting bracket F having a horizontal gear rack f on its upper side. The supporting plate e' is provided centrally on its front side with a forwardly projecting bracket G having a horizontal gear rack g on its under side, which latter is arranged above the gear rack f of the bracket F.

H represents a gear wheel arranged between the brackets F, G, and meshing with both the upper and lower gear racks f, g . This gear wheel is secured to the middle of a transverse shaft I, which latter passes with its ends through slots i formed lengthwise in the longitudinal beams, thereby permitting the shaft and gear wheel to move lengthwise in the press frame.

J represents a lever whereby the foot block is operated. This lever is provided at its lower end with two arms j which straddle the press frame and are secured to opposite ends of the shaft I, while its upper portion is arranged centrally above the press frame.

k represents a vertically movable cross head arranged in rear of the rear cross piece and

guided with its ends in vertical grooves k' formed in the upright members k^2 of a guide frame which is secured to the rear end of the press frame. The cross head is provided with a loop or bail l which is connected with the upper end of the lever J by a rope, chain or cable l' . The latter runs over a pulley m secured to a transverse shaft n journaled with its ends in bearings secured to the upright members k^2 of the guide frame.

o represents a box which rests upon the cross head and is filled with a weighting material.

In the normal position of the parts, the cross head is at its lowest point, the lever J stands upright and the foot block is in its forward position, as represented in Fig. 3, in which position of the parts the cheeses are placed between the head and foot blocks. Upon turning the screw b in the proper direction to apply the preliminary pressure to the cheeses, air and whey are expelled from the cheeses and the foot block is forced back. This backward movement of the foot block causes its gear rack f meshing with the lower side of the gear wheel H to turn the latter and to roll it backwardly on the upper gear rack g . As the upper gear rack is stationary, the backward movement of the gear wheel is equal to one-half of the movement of the foot block. This rotative movement of the foot block swings the lever J forwardly and raises the weighted cross head attached to the lever. When the foot block has reached the limit of its backward movement, the lever J connected with the gear wheel H has been moved forwardly and the weight has been raised, as represented in Fig. 4. After the preliminary pressing of the cheeses has been completed, the pressure which is exerted upwardly upon the lever J by the weighted cross head raises the lever J and moves the foot block forwardly, which causes a constant pressure to be exerted upon the cheeses and whereby the operation of pressing is completed.

When the lever J is depressed it stands at an acute angle to the line in which the pressure is applied to the same by the weighted cross head and the effective force of the weight is comparatively small. As the lever rises, owing to the shrinking of the cheese, the effective leverage gradually increases until the lever J has been raised nearly to a vertical position. By this means the automatic final pressure which is exerted upon the cheeses is continuous and increases gradually as the cheeses become more compact.

In the modified construction represented in Fig. 8, a lever g is substituted for the gear wheel H . This lever is secured to the transverse shaft I and has its upper arm g' connected with the supporting plate e' by a link r , while its lower arm g^2 is connected with the foot block by a link r' .

In the modified construction represented in Fig. 7, the shaft to which the gear wheel is

secured is not movable lengthwise of the press frame, but turns in fixed bearings s which are secured to the rear portion of the press frame.

In the modified construction represented in Fig. 8, my improvement is applied to a press in which two gangs of cheeses are pressed simultaneously. In this construction the shaft carrying the gear wheel is arranged between two movable foot blocks T T' , each of which is provided with a gear rack t t' between which the gear wheel is arranged, so that the two foot blocks approach each other while the preliminary pressure is applied, and recede from each other while the automatic pressure is applied.

It is obvious that a coil spring mounted in a barrel or drum may be substituted for the weight which is applied to the lever by which the automatic pressure is applied to the foot block.

I am aware that it is not new to apply pressure automatically in a cheese press and I do not broadly claim the same. It is also obvious that the entire pressure can be applied by the automatic mechanism, in which case the head block can be made stationary.

I claim as my invention—

1. The combination with the stationary press frame, the movable head block and the screw by which the head block is moved toward the foot block, of a movable foot block, a gear rack secured to the foot block, a gear wheel meshing with said gear rack, and an automatic pressure device whereby said gear wheel is rotated in the direction in which it moves the foot block toward the head block, substantially as set forth.

2. The combination with the stationary press frame, the movable head block and the screw by which the head block is moved toward the foot block, of a movable foot block, a gear rack secured to the foot block, a stationary gear rack secured to the press frame, a gear wheel meshing with both gear racks, and an automatic pressure device whereby said gear wheel is rotated in the direction in which it moves the foot block toward the head block, substantially as set forth.

3. The combination with the press frame and the head block, of a movable foot block provided with a rearwardly projecting gear rack, a supporting plate secured to the press frame and provided with a forwardly projecting gear rack, a transverse shaft provided with a gear wheel meshing with both gear racks, a lever connected at one end with said shaft, and a weight connected with the opposite end of said lever, substantially as set forth.

4. The combination with the press frame, the movable head block and the pressure screw whereby the head block is moved, of a movable foot block provided with a rearwardly projecting gear rack, a forwardly projecting gear rack secured to the press frame, a trans-

verse shaft provided with a gear wheel mesh-
ing with both gear racks, a lever secured with
its lower end to said shaft, a guide frame se-
cured to the press frame and provided with
a pulley, a vertically movable cross head ar-
ranged in said guide frame and provided with
a weight, and a cable connecting the upper
end of said lever with the cross head and
passing around said pulley, substantially as
set forth. 10
Witness my hand this 18th day of June,
1892.

CARL JOHAN LUNDSTROM.

Witnesses:

GEO. B. WHITE,
W. C. FITCH.



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54 Method for breaking emulsions.

57 A method for recovering the surfactant from a dispersion or emulsion of oil and water containing a temperature sensitive surfactant which method comprises the steps of heating the dispersion or emulsion to a temperature above the cloud point of the surfactant under conditions of temperature and aqueous phase salinity such that the dispersion or emulsion breaks and separates into an oil layer, an aqueous layer and a surfactant layer, and recovering the surfactant layer.

The recovered surfactant may be recycled for use in preparing further quantities of dispersion or emulsion, thus rendering the operation more economic.

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METHOD FOR BREAKING EMULSIONS

This invention relates to a method for breaking a dispersion or emulsion of oil and water and recovering the surfactant used in the formation of the dispersion or emulsion.

Emulsions of oil and water are well known. These may be in the form of oil-in-water emulsions (O/W) or water-in-oil emulsions (W/O). In order to prepare stable emulsions, a surfactant is generally employed. This may be a temperature sensitive surfactant, ie, one which is more water soluble at lower temperatures and more oil soluble at higher temperatures.

A particular application of O/W emulsions is in the transportation of crude oil emulsions, particularly emulsions of heavy crude oils which are too viscous in themselves to be pumped through a pipeline. The emulsions may be transported to refineries where they may be broken by the application of heat and separated into oil and aqueous phases, with the oil phase being processed and the aqueous phase discarded as effluent which, however, requires treatment prior to discharge.

Attempts have been, made in the past to recover surfactants from emulsions.

USP 4518038 discloses a process for extracting surfactant from produced emulsions by concentrating the surfactants into a relatively small volume emulsion middle phase (between oil and water phases) which can be re-utilised in surfactant flooding.

This process requires the use of a hydrotropic extracting agent and leaves the surfactant as the major component of a microemulsion.

To the best of our knowledge, no method has yet been devised for recovering the surfactant from broken emulsions without the use of an extracting agent. This, therefore, represents a considerable economic loss and, in addition, the surfactant if present in the aqueous phase can give rise to effluent treatment problems and the surfactant if present in the oil may have undesirable repercussions on subsequent refining processes.

When an emulsion containing a temperature sensitive surfactant is broken at elevated temperature one might expect that the surfactant would tend to pass predominantly from the aqueous phase into the oil phase with perhaps the formation of an intermediate layer containing oil, water and a relatively high concentration of surfactant.

We have surprisingly discovered that under certain conditions this does not happen, and the surfactant, instead, separates out as a distinct, dense layer below the aqueous layer, which can readily be recovered and re-used.

The reasons for this effect are not yet fully understood but it is believed that important parameters affecting it include the temperature at which the emulsion is broken, the viscosity of the oil phase at this temperature, the salinity of the aqueous phase, and the relative densities of the oil, water and surfactant phases.

Thus according to the present invention there is provided a method for recovering the surfactant from a dispersion or emulsion of oil and water containing a temperature sensitive surfactant which method comprises the steps of heating the dispersion or emulsion to a temperature above the cloud point of the surfactant under conditions of temperature and aqueous phase salinity such that the dispersion or emulsion breaks and separates into an oil layer, an aqueous layer and a surfactant layer, and recovering the surfactant.

The recovered surfactant may be recycled for use in preparing further quantities of dispersion or emulsion, thus rendering the process more economic.

The temperature, the salinity, and also the oil droplet size are interrelated and certain guidelines have been established. Within these guidelines, operating conditions for any given dispersion or emulsion can be determined by simple experiments.

In general, the ease with which a dispersion or emulsion can be resolved into three components depends on the oil droplet size, the salinity of the aqueous phase and the temperature.

The presence of a salt, eg, sodium chloride, even in small quantities, encourages the separation of the surfactant layer and therefore this is preferably added, if not initially present.

In practice, if dispersions or emulsions are made in the field from crude oil and co-produced connate water, it will frequently be unnecessary to add salt since the connate water itself will often contain sufficient quantity.

The age of the dispersion or emulsion is perhaps also significant. The younger it is, the easier it is likely to be to resolve it.

Suitable temperatures will generally be found in the range 100° -140° C and suitable salinities in the range 0.1 to 1% by weight of the aqueous phase.

Although dispersions may be treated in the above manner, the method is particularly applicable to the treatment of emulsions, especially emulsions of the oil-in water type.

The oil is preferably a hydrocarbon oil, although non-hydrocarbon oils may be used. Particularly suitable oils include crude oils, especially the viscous, heavy and/or asphaltenic crude oils to be found in Canada, the USA and Venezuela; for example, Lake Marguerite and Wolf Lake crude oils from Alberta, Hewitt crude oil from Oklahoma and Cerro Negro bitumen from the Orinoco Oil Belt.

Preferably the API gravity of the crude oil is in the range 5° to 20°, although the method can be applied to emulsions of crude oils outside this API range.

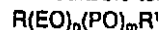
The invention is particularly applicable to the recovery of surfactants from HIPR (High Internal Phase Ratio) emulsions of viscous crude oils in water, including diluted HIPR emulsions. The preparation of such emulsions and their subsequent dilution is disclosed in European patent application 0156486-A2.

The method comprises directly mixing 70 to 98% by volume of a viscous oil having a viscosity in the range 200 to 250,000 mPa.s at the mixing temperature with 30 to 2% by volume of an aqueous solution of an emulsifying surfactant, percentages being expressed by volume of the total mixture, mixing being effected under low shear conditions in the range 10 to 1,000 reciprocal seconds in such manner that an emulsion is formed comprising distorted oil droplets having mean droplet diameters in the range 2 to 50 micron separated by interfacial films.

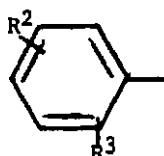
The HIPR emulsions as prepared are stable and can be diluted with aqueous surfactant solution, fresh water or saline water to produce emulsions of lower oil phase volume showing high degrees of monodispersity. The emulsions may be diluted to a required viscosity without adversely affecting stability. Because the narrow size distribution and droplet size are maintained upon dilution the resulting emulsion shows little tendency to creaming. It is also important that the viscous oil and water have similar densities. These factors reduce the risk of phase separation occurring.

The emulsions, particularly when diluted, are suitable for transportation through a pipeline.

Suitable temperature sensitive surfactants can be represented by the formula:



wherein R is a branched or unbranched alkyl group containing 4 to 20 carbon atoms or an alkyl phenyl group of formula:



wherein R² is a branched or unbranched alkyl group containing 1 to 20 carbon atoms and R³ is a hydrogen atom,

or R² and R³ are both branched or unbranched alkyl groups containing 1 to 20 carbon atoms,

EO is an ethylene oxide group,

PO is a propylene oxide group,

n is a number in the range 1 to 50, preferably 5 to 25, m is a number in the range 0 to 20,

R¹ is an -OH radical, a sulphate or a sulphonate group.

The preferred surfactants are alkyl phenol ethoxylates, most preferably nonyl phenol ethoxylates, containing approximately 15 to 30 ethylene oxide groups per molecule, most preferably about 20.

The surfactants are suitably employed in amount 0.1 to 5% by weight expressed as a percentage by weight of the aqueous phase of the emulsion.

Asphaltenes, porphyrins and similar high molecular weight compounds, if present in the oil, may precipitate in association with the surfactant, and thus dispersion breaking or emulsion breaking may simultaneously effect deasphalting and demetallisation of the oil.

Such compounds can easily be removed from the surfactant, thus rendering the latter suitable for re-use.

According to another aspect of the present invention there is provided a method for the transportation of a viscous oil which method comprises the steps of

(a) directly mixing 70 to 98%, preferably 50 to 90%, by volume of a viscous oil having a viscosity in the range 200 to 250,000 mPa.s, preferably 2,000 to 250,000 mPa.s, at the mixing temperature with 30 to 2%, preferably 20 to 10%, by volume of an aqueous solution of a temperature sensitive surfactant, percentages being expressed as percentages by volume of the total mixture; mixing being effected

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under low shear conditions in the range 10 to 1,000, preferably 50 to 250, reciprocal seconds in such manner that an HIPR emulsion is formed comprising distorted oil droplets having mean droplet diameters in the range 2 to 50 micron separated by interfacial films,

- 5 (b) diluting the HIPR emulsion with an aqueous phase to a desired viscosity and concentration, eg to an emulsion containing 30 -50% by volume of the aqueous phase,
- (c) transporting the diluted emulsion through a pipeline,
- (d) heating the diluted emulsion to a temperature above the cloud point of the surfactant under conditions of temperature and aqueous phase salinity such that the diluted emulsion breaks and separates into an oil layer, an aqueous layer and a surfactant layer,
- 10 (e) recovering the surfactant layer, and
- (f) recycling the recovered surfactant by dissolving it in water and utilising the resulting solution in Step (a).

The invention is illustrated by but not limited with reference to the following Examples and Figures 1A, 1B, 2A, 2B and 3 of the accompanying drawings.

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Examples

- 20 Wolf Lake crude oil (WLCO) having an API Gravity of 10.3°, was used as the heavy oil phase in both the neat form and blended with 30% naphtha as a diluent. The surfactant, NP20, was a nonylphenol ethoxylate containing an average of 20 moles of ethylene oxide per molecule. The salt was sodium chloride.

The HIPR derived emulsions of Examples 2 and 3 stabilised with 2.5 or 5wt% NP20 in the aqueous phase were prepared by the two stage method described in EP 0158488-A2. The coarse dispersion of
25 Example 1 was prepared in the same equipment but in one stage using a 50/50 blend of oil and aqueous phase.

Phase Behaviour Studies

30

Samples of the relevant heavy oil and aqueous phases were sealed in phase tubes (total volume ca 12ml) made from 10ml graduated glass pipettes. These tubes were then incubated at the required temperature (typically > 90°C) in an oven fitted with an observation window, and the phase
35 behaviour/emulsion resolution monitored for 24 hours. The series of systems examined in this study are given in Table 1.

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Table 1

Example	Phase volume (ml)		Aqueous phase Composition (wt%)		Comments
	Oil	Aqueous	Surfactant	Salt	
1A 1B 1C	5	5	2.5	0	Coarse dispersion of WLCO in relevant aqueous phases
				0.1	
				0.5	
1D				1.0	
1E 1F 1G 1H	5	5	5.0	0	
				0.1	
				0.5	
				1.0	
2A 2B 2C	6.5	3.5	2.5	0	65wt% HIPR-derived WLCO-in-water emulsion used
				0.1	
				0.5	
2D				1.00	
2E 2F 2G 2H	6.5	3.5	5.0	0	
				0.1	
				0.5	
				1.0	
3A 3B 3C 3D	7.5	2.5	2.5	0	1:1 (v/v) mixture of 50% HIPR derived WLCO-in-water emulsion and WLCO/blend
				0.1	
				0.5	
				1.0	
3E 3F 3G 3H	7.5	2.5	5.0	0	
				0.1	
				0.5	
				1.0	

Example 1

Coarse dispersions were prepared of WLCO in aqueous phases containing the concentrations of surfactant and salt set out in Table 1 and the phase separation investigated at temperatures of 90° and 105° C.

At 90° C the effect of a prolonged incubation time was merely to promote separation of the oil and water phases into an upper layer of oil and a lower aqueous layer with no surfactant separation. However, at the higher temperature, substantial differences resulting from the different salt concentrations were apparent. Although there was little effect of salt concentration on the overall phase separation process, differences in the quality of the aqueous phase were revealed at the higher temperature, with the presence of salt clearly an advantage. For this system a temperature of 105° C was sufficient to promote surfactant phase separation into a third layer below the water layer.

The phase separation behaviour of this system is illustrated in Figures 1A and 1B. The clear area represents the oil phase, the wide hatching the aqueous phase and the narrow hatching the surfactant phase. Figure 1A represents the behaviour of the system containing 2.5% NP20 and Figure 1B the system containing 5% NP20.

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Example 2

HIPR emulsions were prepared of WLCO in aqueous phases containing the concentrations of surfactant and salt set out in Table 1 and the phase separation investigated at temperatures of 105° and 125° C.

- 5 In contrast to the behaviour observed for the coarse dispersion, the emulsion system required the higher temperature of 125° C to induce efficient phase separation into the three layers although emulsion resolution commenced at 105° C. In this system also, the presence of salt in the aqueous phase improved the quality of the separated aqueous phase for both surfactant concentrations.

The phase separation behaviour of this system is illustrated in Figures 2A and 2B. In this case, the clear
10 area represents the oil or emulsion phase, the wide hatching the aqueous phase and the narrow hatching the surfactant phase. Figure 2A represents the behaviour of the system containing 2.5% NP 20 and Figure 2B the system containing 5% NP 20.

Example 3

In an attempt to simulate the co-treatment of WLCO emulsions and blended WLCO (ie, containing a diluent), at, for example, a refinery, the high temperature phase separation/resolution of a 1:1 (by volume) mixture was examined as described above for Example 2.

- 20 The behaviour was analogous to the behaviour of the emulsion itself, allowing for the reduced volume of the separated water and surfactant phases. Also consistent with the previous examples was the beneficial effect that the presence of salt had on the quality of the separated water.

The phase separation behaviour of this system is illustrated in Figure 3, with the same symbolism as for Figure 2. Figure 3 represents the behaviour of the system containing 5% NP 20.

- 25 These results demonstrate the separation of surfactant in the presence of salt in the region of 100° - 130° C. In the presence of heavy oil, the temperature at which surfactant separation occurs varies slightly, depending on whether the oil is coarsely dispersed or emulsified. Of significance is the effect of salt concentration, in which the effects of even a low concentration of salt are evident.

Heating a coarse dispersion of a heavy oil in aqueous NP20 solutions to temperatures in excess of
30 100° C promotes the separation of a dense surfactant-rich phase.

When the heavy oil is present as emulsified droplets the emulsion is simultaneously broken when the surfactant phase separates.

Emulsion resolution and surfactant phase separation also occur for mixtures of blended and emulsified heavy oil.

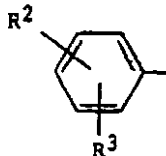
Claims

1. A method for recovering the surfactant from a dispersion or emulsion of oil and water containing a
40 temperature sensitive surfactant characterised by the fact that the method comprises the steps of heating the dispersion or emulsion to a temperature above the cloud point of the surfactant under conditions of temperature and aqueous phase salinity such that the dispersion or emulsion breaks and separates into an oil layer, an aqueous layer and a surfactant layer, and recovering the surfactant layer.
2. A method according to claim 1 wherein the dispersion or emulsion is heated to a temperature in the
45 range 100° -140° C.
3. A method according to either of the preceding claims wherein the aqueous phase contains 0.1 to 1% by weight salt.
4. A method according to any of the preceding claims wherein the oil is a crude petroleum oil.
5. A method according to claim 4 wherein the crude oil has an API gravity in the range 5 - 20°.
- 50 6. A method according to claim 5 wherein the emulsion is an HIPR emulsion or derived from an HIPR emulsion.
7. A method according to claim 6 wherein the HIPR emulsion is prepared by directly mixing 70 to 98% by volume of a viscous oil having a viscosity in the range 200 to 250,000 mPa.s at the mixing temperature with 30 to 2% by volume of an aqueous solution of an emulsifying surfactant, percentages being expressed as
55 percentages by volume of the total mixture, mixing being effected under low shear conditions in the range 10 to 1,000 reciprocal seconds in such manner that an emulsion is formed comprising distorted oil droplets having mean droplet diameters in the range 2 to 50 micron separated by interfacial films.
8. A method according to any of the preceding claims wherein the temperature sensitive surfactant is

represented by the formula:



wherein R is a branched or unbranched alkyl group containing 4 to 20 carbon atoms or an alkyl phenyl group of formula:



wherein R² is a branched or unbranched alkyl group containing 1 to 20 carbon atoms and R³ is a hydrogen atom,

or R² and R³ are both branched or unbranched alkyl groups containing 1 to 20 carbon atoms,

EO is an ethylene oxide group,

PO is a propylene oxide group,

n is a number in the range 1 to 50,

m is a number in the range 0 to 20, and

R¹ is an -OH radical, a sulphate or a sulphonate group.

9. A method according to claim 8 wherein the temperature sensitive surfactant is an alkyl phenol ethoxylate containing 15 - 30 ethylene oxide groups per molecule.

10. A method according to claim 9 wherein the temperature sensitive surfactant is a nonyl phenol ethoxylate containing 20 ethylene oxide groups per molecule.

11. A method according to any of the preceding claims wherein the surfactant is used in amount 0.1 to 5% by weight of the aqueous phase of the emulsion.

12. A method for the transportation of a viscous oil which method comprises the steps of

(a) directly mixing 70 to 98%, by volume of a viscous oil having a viscosity in the range 200 to 250,000 mPa.s, at the mixing temperature with 30 to 2%, by volume of an aqueous solution of a temperature sensitive surfactant, percentages being expressed as percentages by volume of the total mixture; mixing being effected under low shear conditions in the range 10 to 1,000 reciprocal seconds in such manner that an HIPR emulsion is formed comprising distorted oil droplets having mean droplet diameters in the range 2 to 50 micron separated by interfacial films,

(b) diluting the HIPR emulsion with an aqueous phase to a desired viscosity and concentration,

(c) transporting the diluted emulsion through a pipeline,

(d) characterised by the fact that the diluted emulsion is heated to a temperature above the cloud point of the surfactant under conditions of temperature and aqueous phase salinity such that the diluted emulsion breaks and separates into an oil layer, an aqueous layer and a surfactant layer,

(e) the surfactant layer is recovered, and

(f) the recovered surfactant is recycled by dissolving it in water and utilising the resulting solution in Step (a).

13. A method according to claim 11 wherein the HIPR emulsion is diluted to an emulsion containing 30 - 50% by volume of the aqueous phase.

FIG. 1A

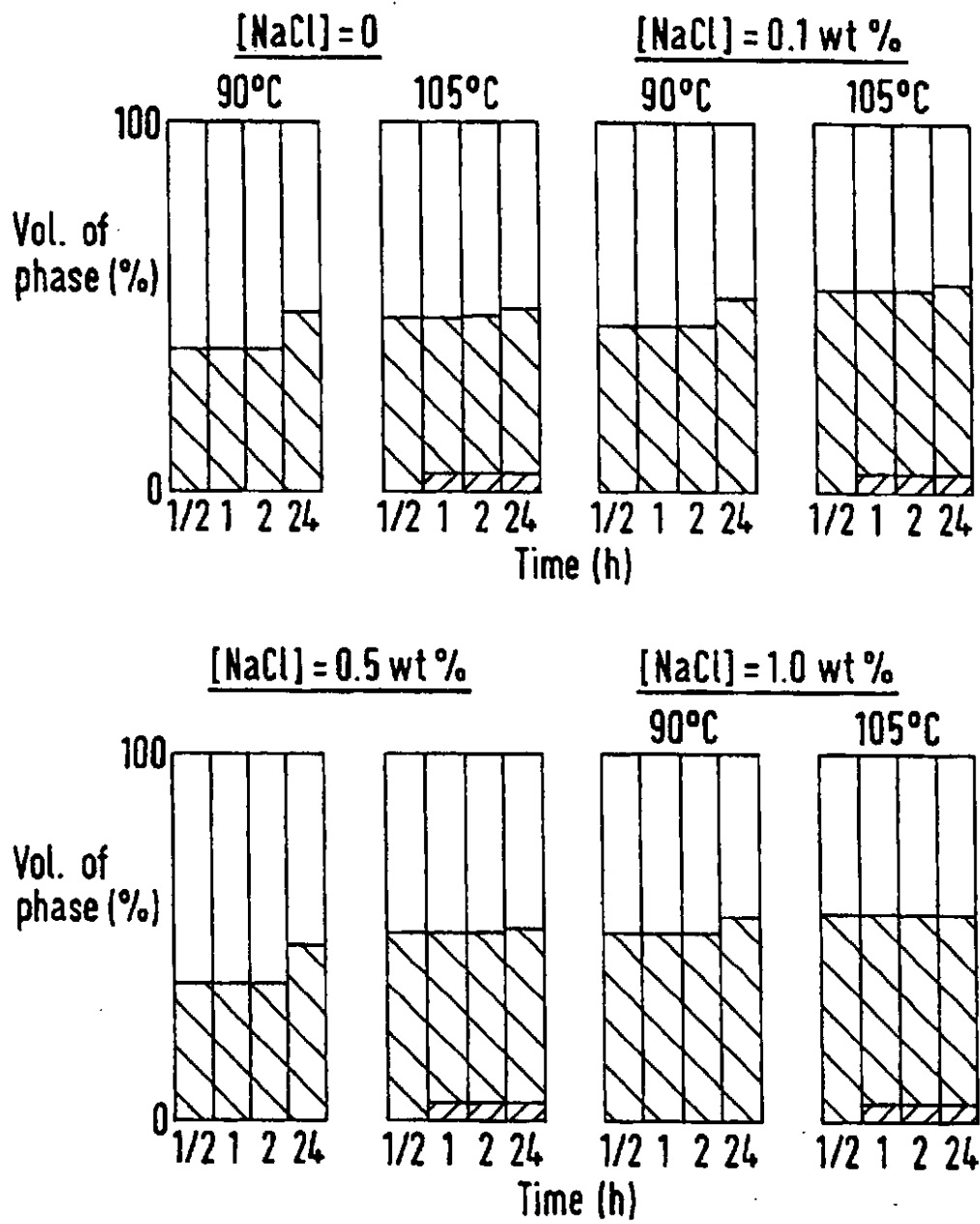


FIG. 1B

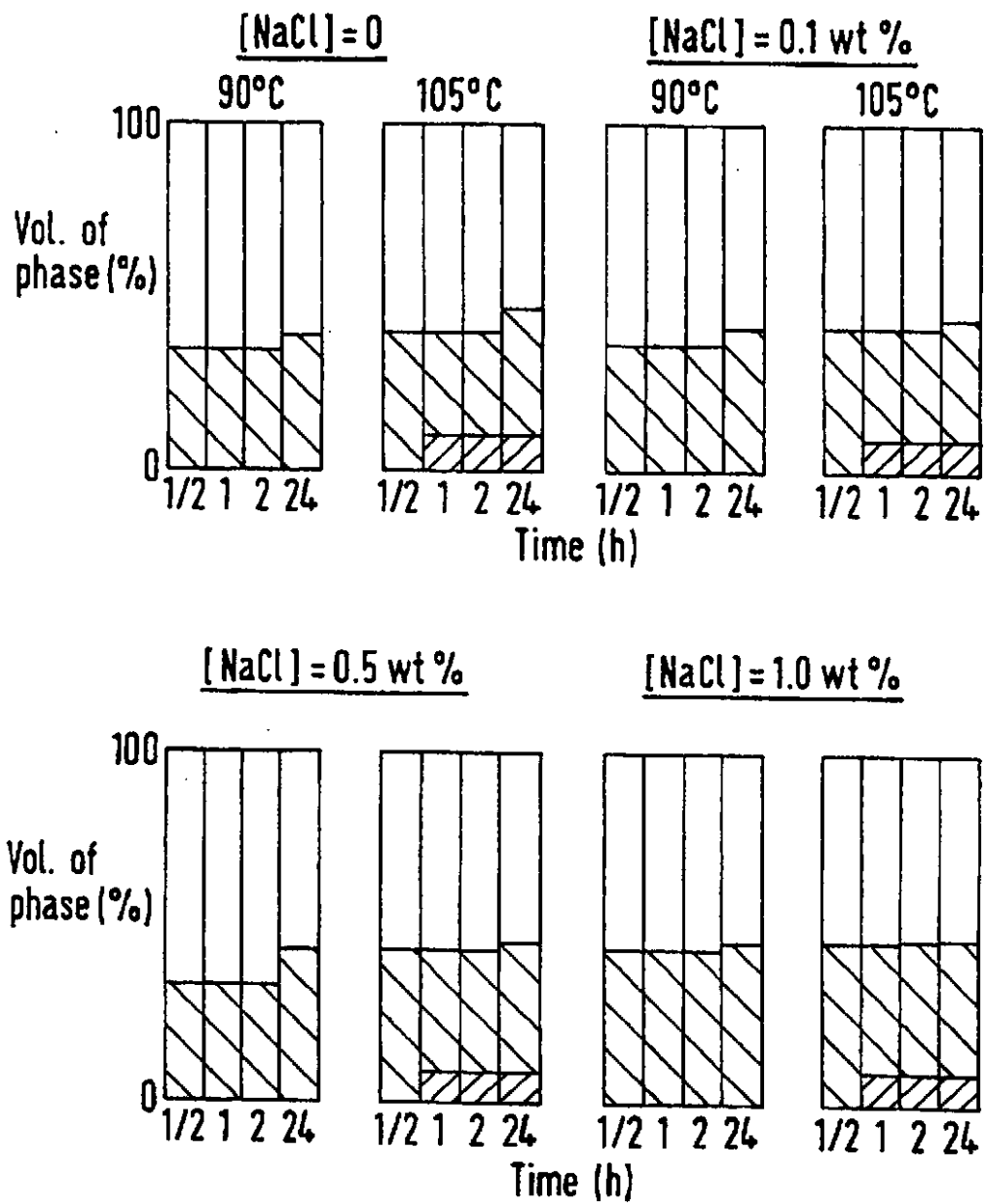


FIG. 2A

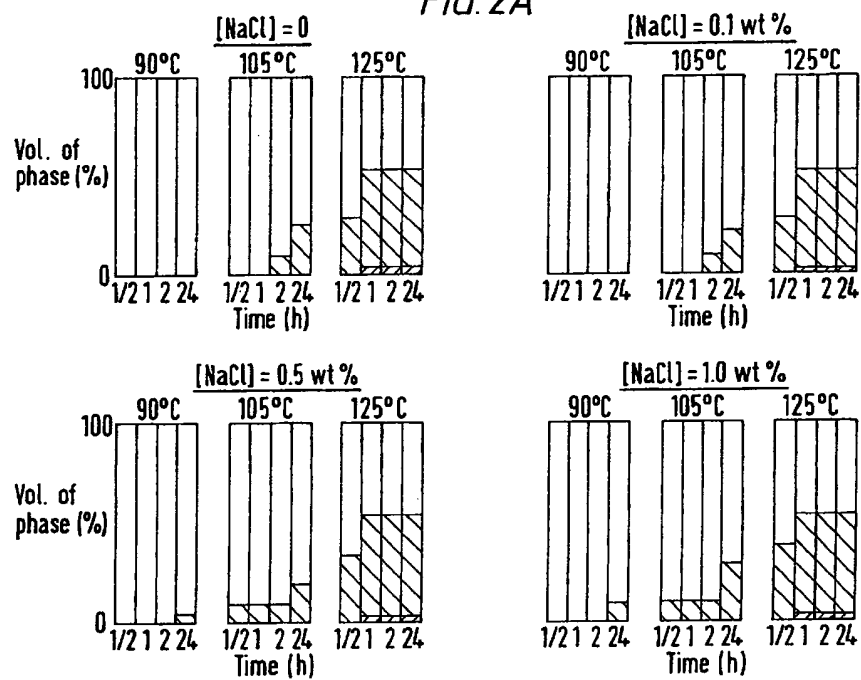


FIG. 2B

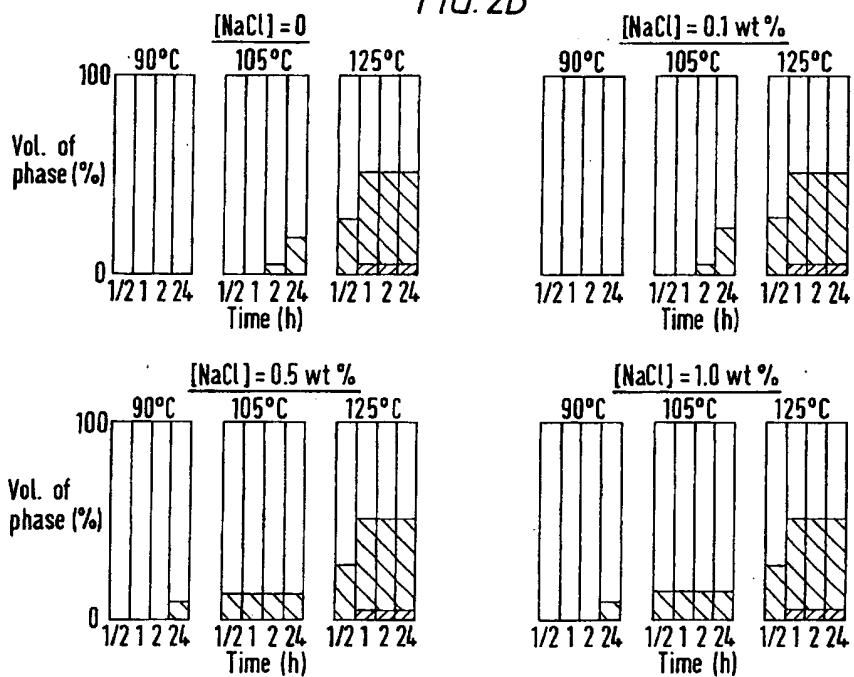
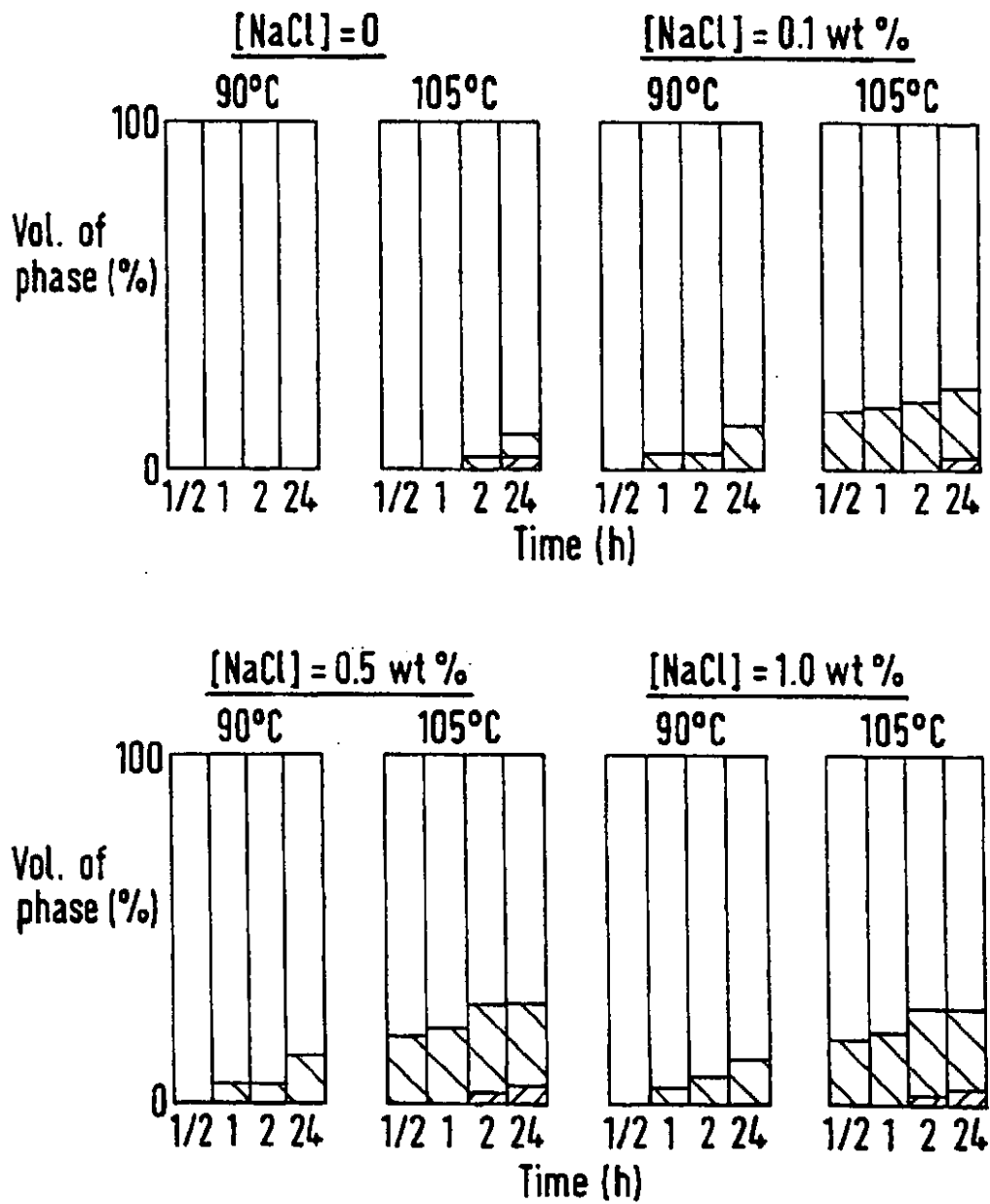


FIG. 3





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Method for breaking emulsions.

A method for recovering the surfactant from a dispersion or emulsion of oil and water containing a temperature sensitive surfactant which method comprises the steps of heating the dispersion or emulsion to a temperature above the cloud point of the surfactant under conditions of temperature and aqueous phase salinity such that the dispersion or emulsion breaks and separates into an oil layer, an aqueous layer and a surfactant layer, and recovering the surfactant layer.

The recovered surfactant may be recycled for use in preparing further quantities of dispersion or emulsion, thus rendering the operation more economic.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 8937

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claims	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
1	X GB-A-2 146 040 (EXXON PRODUCTION RESEARCH CO.) * Page 1, lines 5-7; page 1, line 54 - page 2, line 10; page 2, lines 16-18,50-59; page 5, lines 6-12; claims 1,5 *	1,2,4	B 01 D 17/04
	Y	12	
3	A US-A-4 444 654 (CARGLE et al.) * Column 2, lines 5-32; claim 1 *	1,2,4	
5	A DE-A-2 321 749 (DURKOPPWERKE GmbH) * Page 3, last paragraph - page 4, paragraph 1; claims 1,2 *	1,2	
5	Y US-A-3 491 835 (GAGLE) * Column 1, lines 12-23; column 4, lines 22-33; claims 1,2 *	12	
	A	5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B 01 D C 10 G
The present search report has been drawn up for all claims.			
Place of search THE HAGUE		Date of completion of the search 04-02-1991	Examiner MARZENKE J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : oral-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	

LPO FORM 1503 (01/91)



European Patent
Office

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

X LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1-6: Recovering a surfactant from an emulsion by breaking the emulsion.
Claims 12-13: Method for the transportation of a viscous oil.
2. Claims 7-11: Preparing an emulsion using an emulsifying surfactant.

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims: 1-6, 12-13.



US005863301A

United States Patent [19]
Grosso et al.

[11] Patent Number: 5,863,301
[45] Date of Patent: Jan. 26, 1999

[54] METHOD OF PRODUCE LOW VISCOSITY
STABLE CRUDE OIL EMULSION

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Piedecuesta; Rigoberto Barrero,
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[21] Appl. No.: 778,557

[22] Filed: Jan. 3, 1997

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 253,148, Jun. 2, 1994,
abandoned.

[51] Int. Cl.⁶ C10L 1/32

[52] U.S. Cl. 44/301; 44/301; 44/302;
137/13; 252/312; 507/937

[58] Field of Search 44/301, 302

[56] References Cited

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4,757,833 7/1988 Danley 137/13
5,000,872 3/1991 Olah 252/314
5,013,462 5/1991 Danley 252/8.554
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Primary Examiner—Ellen M. McAvoy

Attorney, Agent, or Firm—Cooper & Dunham LLP

[57] ABSTRACT

A heavy hydrocarbon, oil-in-water emulsion that has a relatively low viscosity for improved transport is disclosed. The emulsion is produced by combining the heavy hydrocarbon with an aqueous solution of emulsifier with agitation. The emulsifier has an HLB value of about 13 to about 16. The emulsifier can be anionic, nonionic, amphoteric, or a mixture thereof. Stirring is effected at medium shear values of about 0.1 sec^{-1} to about 20 sec^{-1} and at a mixer speed of 50 to 2000 rpm. The mixer imparts sufficient power and shear to the emulsion so that a mean oil droplet size of about $30 \mu\text{m}$ is obtained.

23 Claims, 15 Drawing Sheets

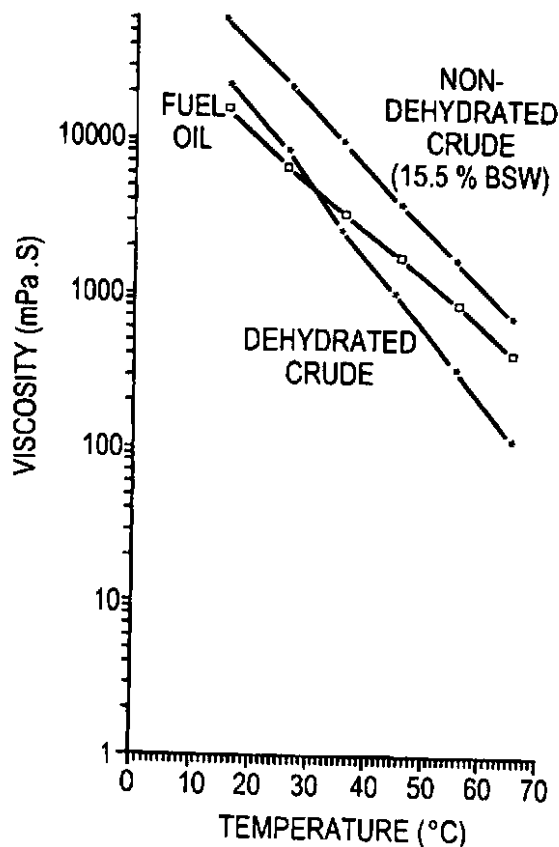


Fig. 1

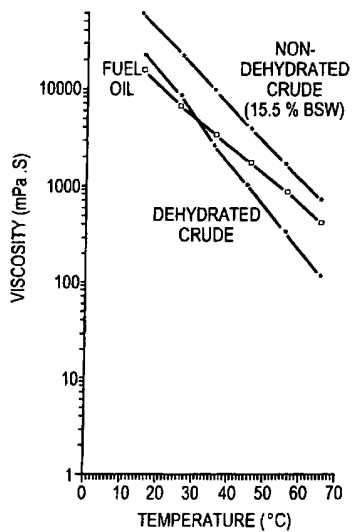


Fig. 2

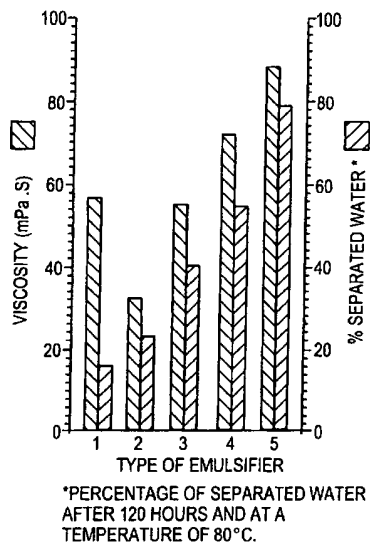


Fig. 4

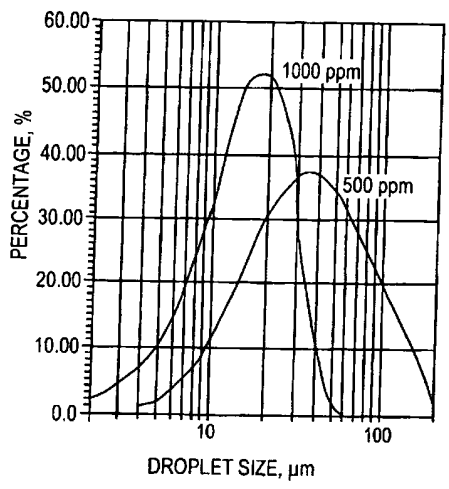
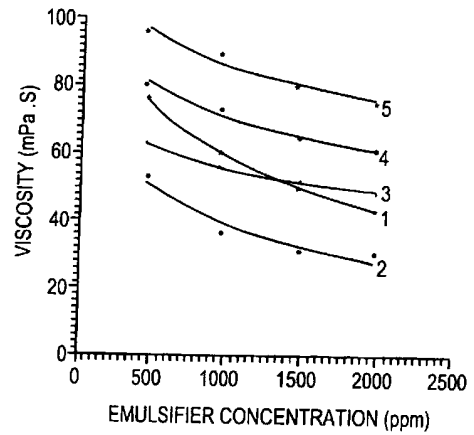


Fig. 3



24

Fig. 5

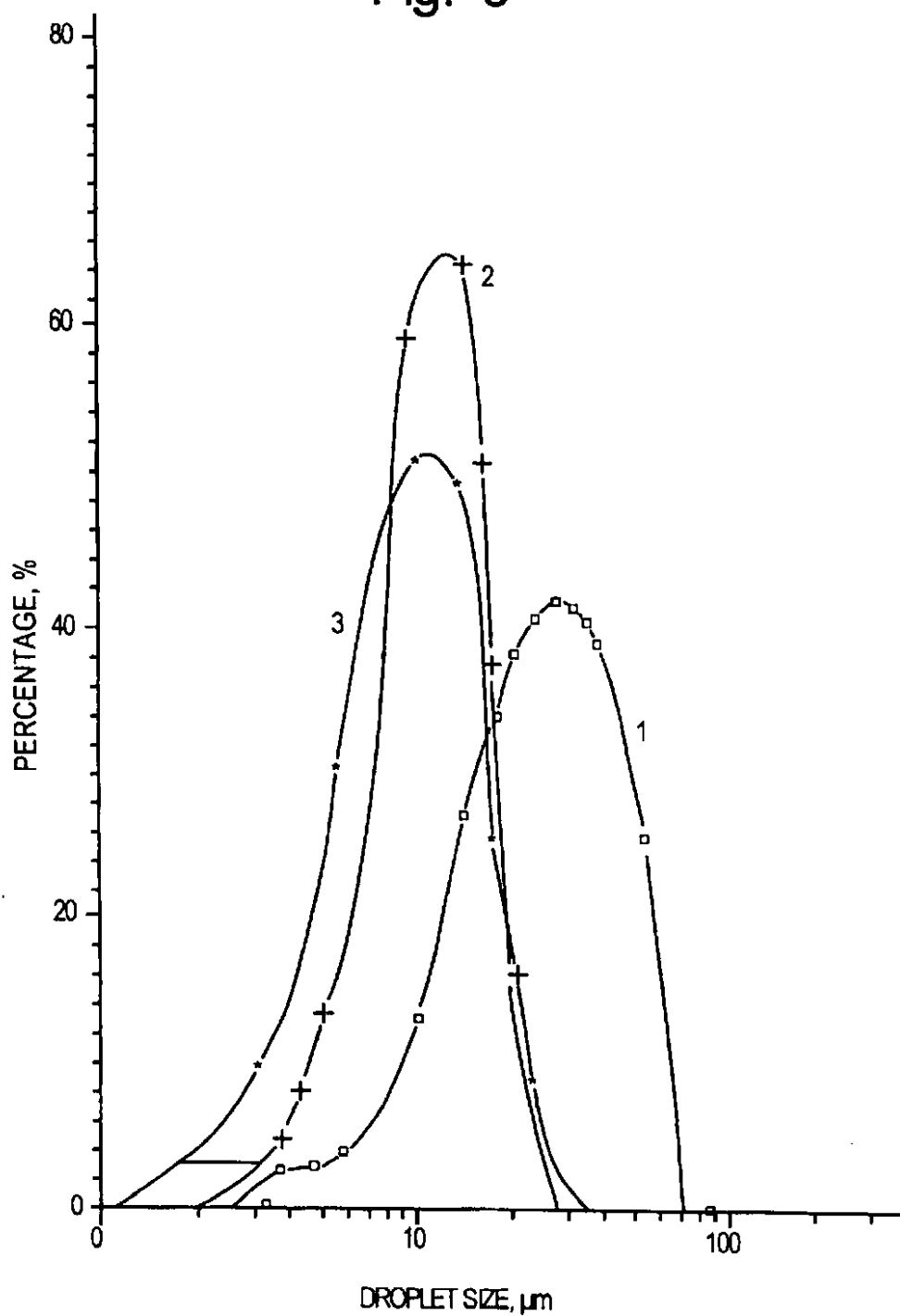


Fig. 6

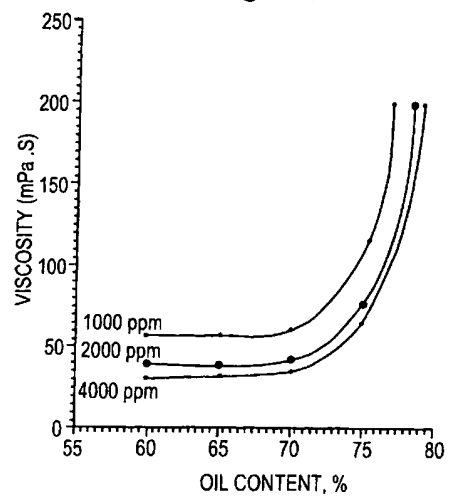


Fig. 7

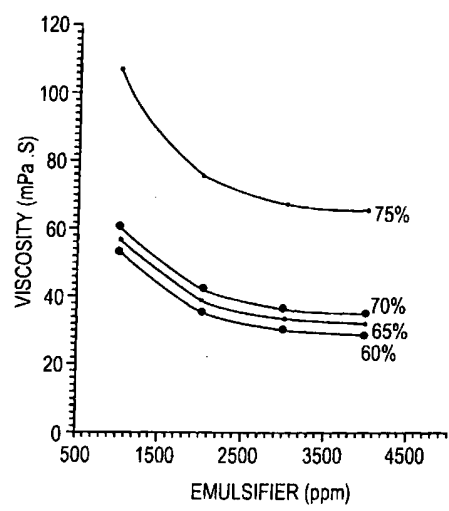


Fig. 8

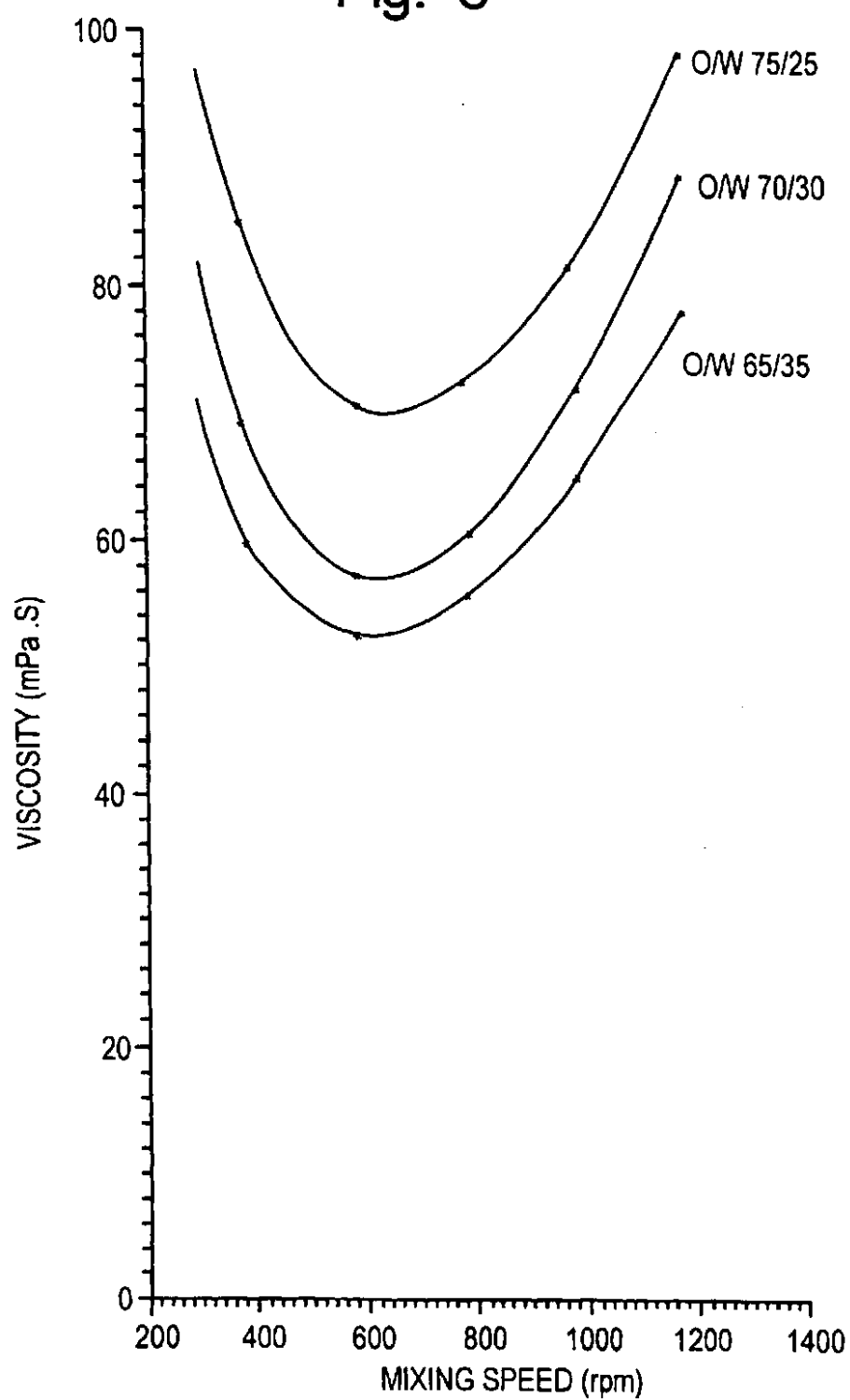


Fig. 10

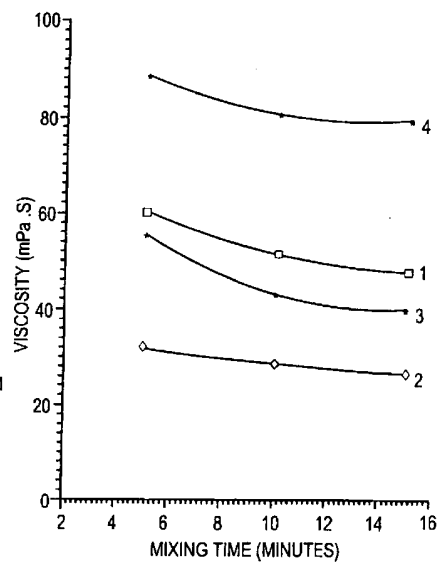


Fig. 9

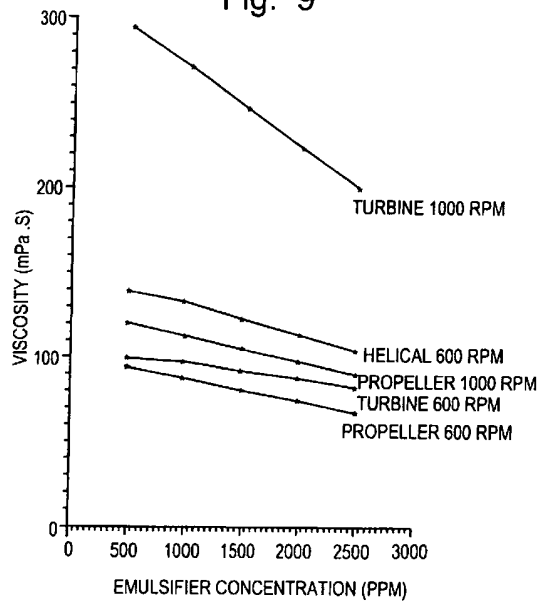


Fig. 11

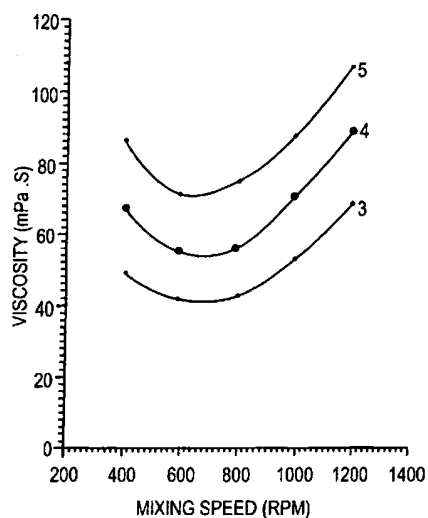


Fig. 12

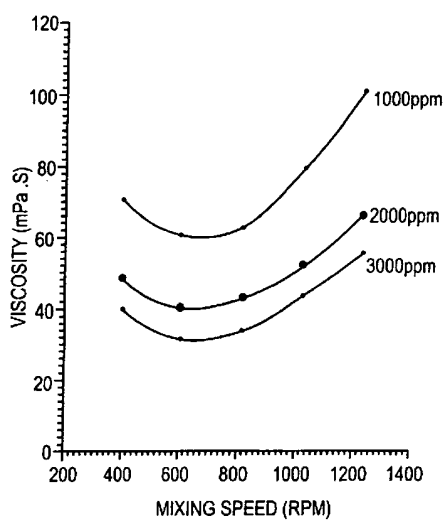


Fig. 13

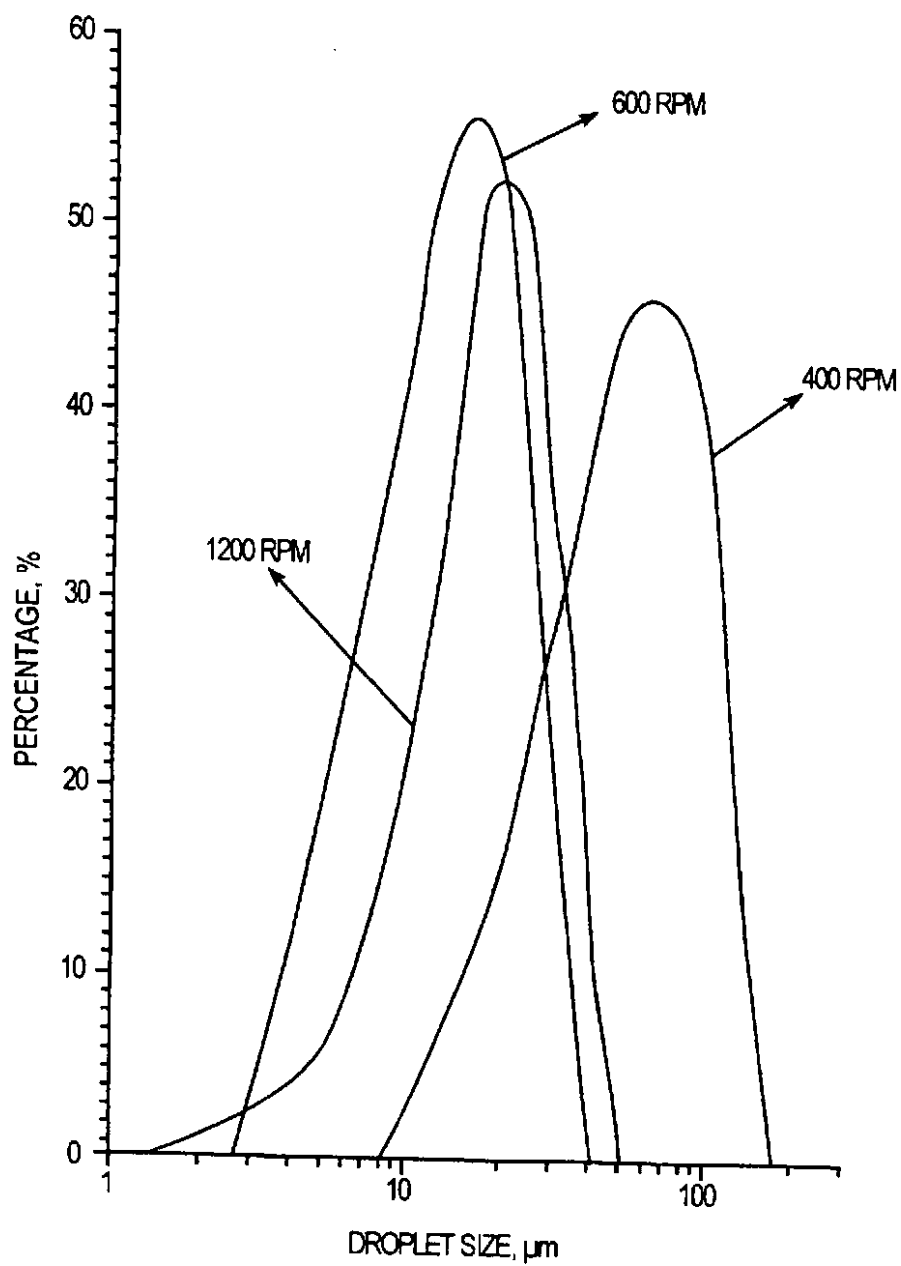


Fig. 14

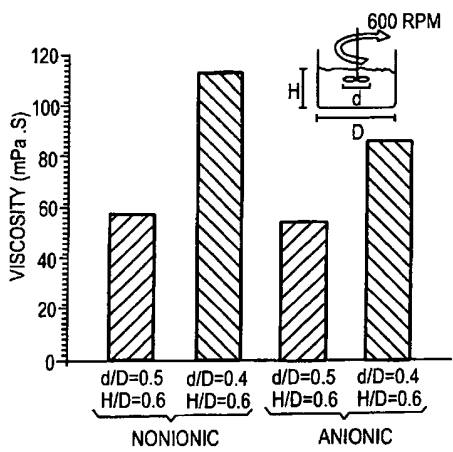


Fig. 15

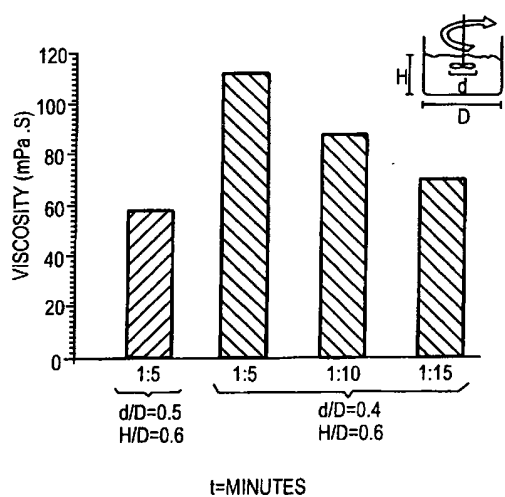


Fig. 16

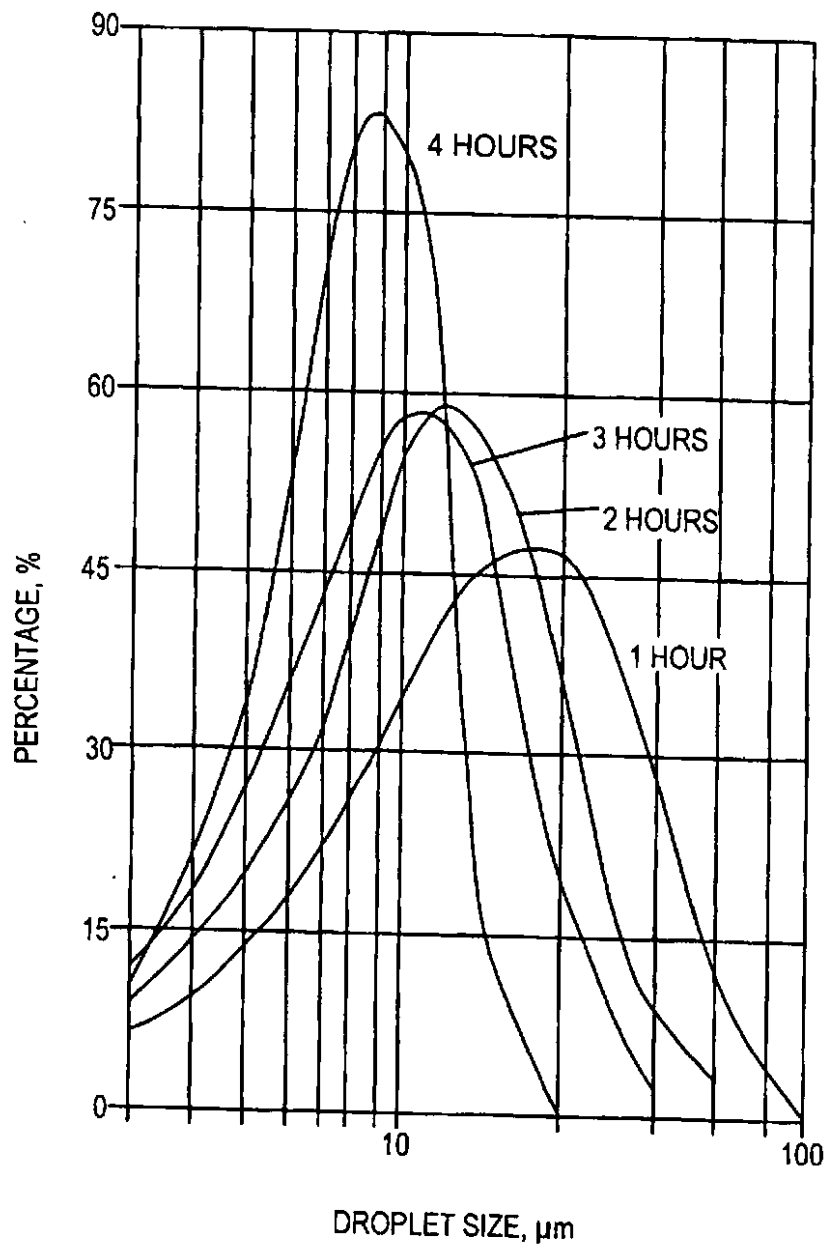
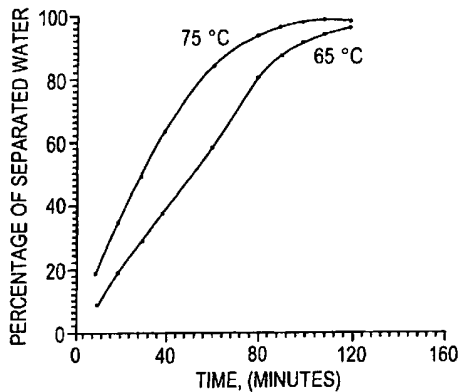
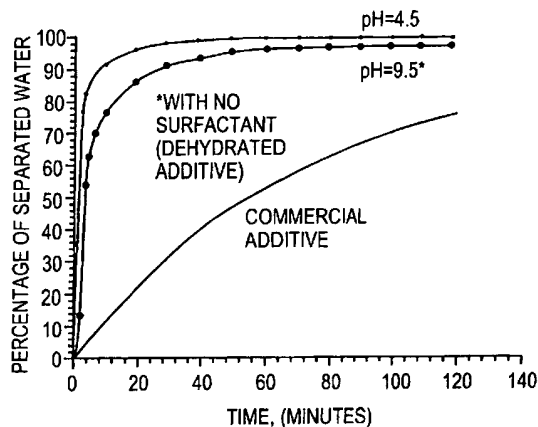


Fig. 17



INFLUENCE OF TEMPERATURE ON O/W EMULSIONS STABILITY

Fig. 18



INFLUENCE OF pH AND EFFECT OF AN EMULSION-BREAKER SURFACTANT ON O/W EMULSIONS STABILITY

Fig. 20

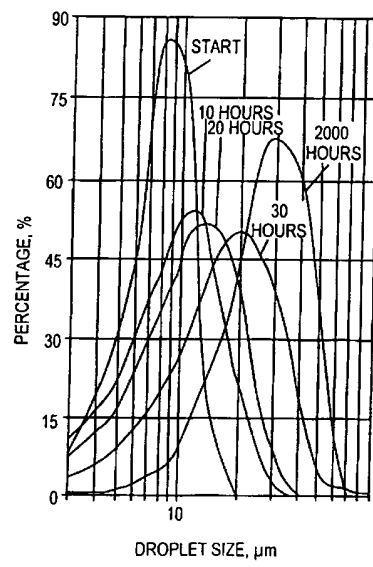


Fig. 19

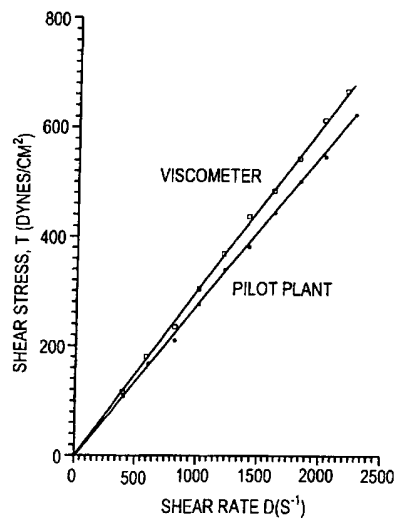


Fig. 21

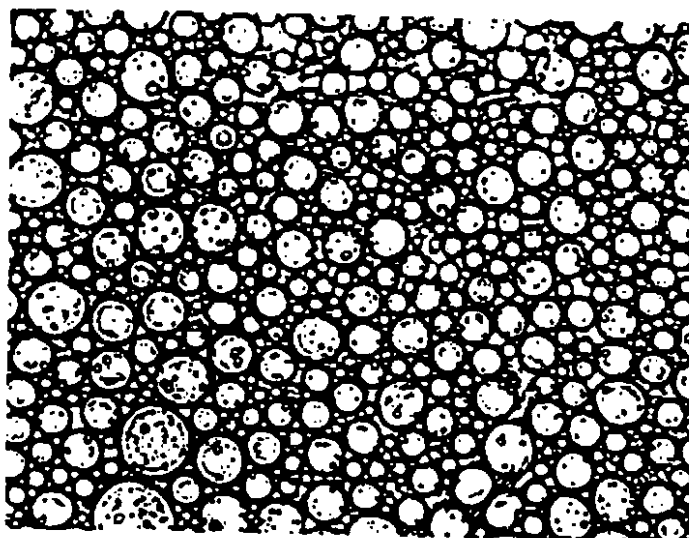


Fig. 22

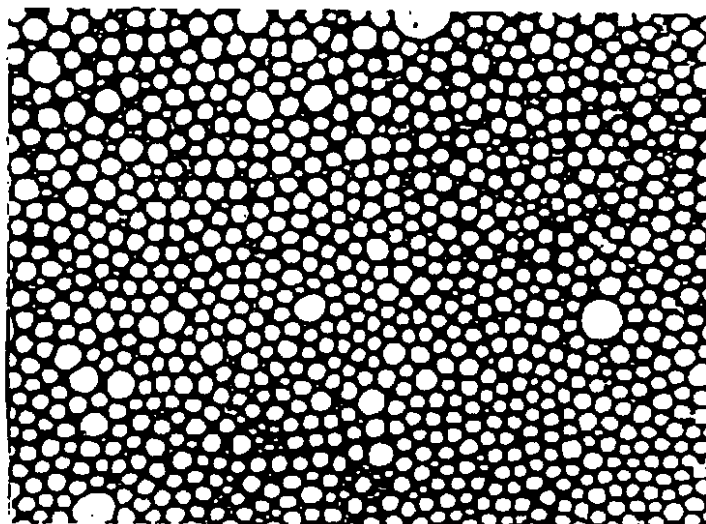


Fig. 23

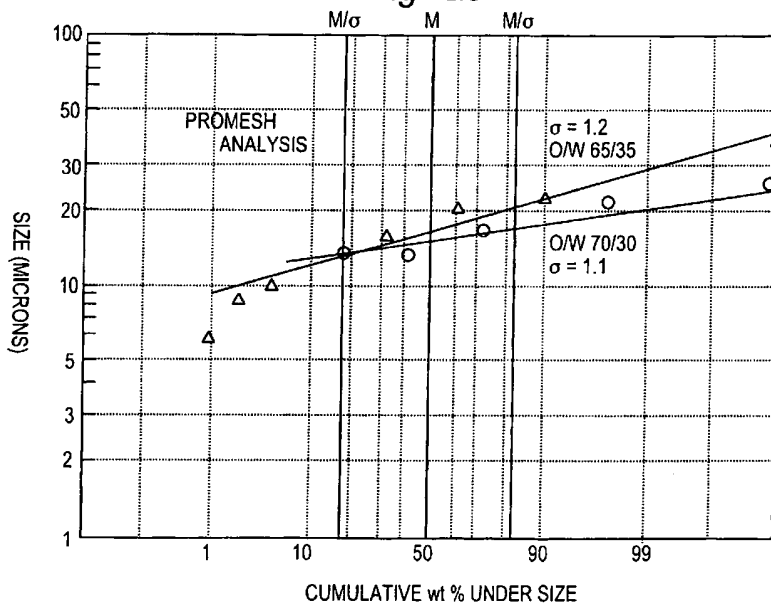


Fig. 24

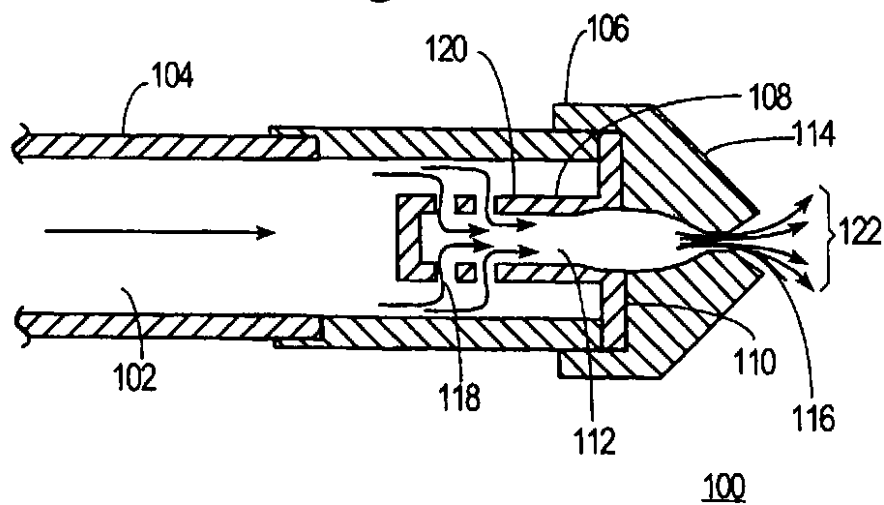
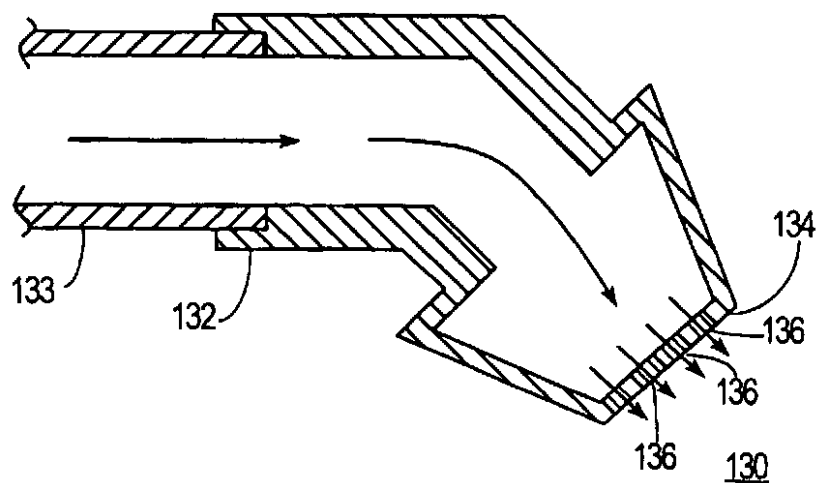


Fig. 25



METHOD OF PRODUCE LOW VISCOSITY STABLE CRUDE OIL EMULSION

This is a continuation-in-part of application Ser. No. 08/253,148 filed Jun. 2, 1994, now abandoned.

TECHNICAL FIELD

The invention is directed to heavy crude oil emulsions, fuel oil emulsions, and the like, and the preparation thereof. Such emulsions have a substantially uniform oil droplet size, are well suited for transportation of heavy crude through pipelines, and are directly combustible as a fuel.

BACKGROUND OF THE INVENTION

The movement of heavy crude through pipelines is difficult. The pumping of heavy crude, fuel oil, and the like is difficult because of the high viscosity of these materials and their resulting low mobility. A known method in the prior art for transporting these heavy, viscous crudes is the addition of lighter hydrocarbons, etc. to the heavy, viscous crudes by a technique such as distillate blending. This technique is expensive as it requires the addition of expensive, light crudes to transport the heavy, less valuable crude. Also, light crudes are more difficult to obtain than the heavy crudes.

Another known method for the transport of heavy, viscous crude is by heating the crude at frequent intervals along the pipeline. This method requires expensive heating equipment to be installed along the pipeline, and also requires maintenance of this equipment. This method also results in a loss of production that can amount to 15% or more of the crude being transferred, the loss resulting from the crude or other energy source utilized to heat the crude.

Yet another method involves the pumping of viscous hydrocarbon through a pipeline surrounded by a lighter viscosity liquid, such as water. In such cases the pressure drop through the pipeline is substantially that of the lighter viscosity liquid. This method of transportation has several disadvantages, however. The major disadvantage is the loss in core flow stability while being pumped over long distances. Slope changes, pipeline diameter changes, transport through booster or repumping stations, and the like expedients are all detrimental to stability. Also, if flow ceases for any reason, the fluid becomes very difficult to pump when transport is resumed, as the core intermixes with the outer layer once the flow of the fluid is ceased or otherwise interrupted.

The use of emulsions to transport heavy crude is also known in the art. Emulsions are typically prepared by adding a mixture of surfactant, blend of surfactants, stabilizer, corrosion inhibitor, pour point depressor and alkaline or neutral pH water to the heavy crude. However, these prior art emulsions fail to optimally reduce viscosity and improve stability of the emulsion while the emulsion is being transported through the pipeline.

Also, conventional systems prepare the heavy crude oil emulsion by conventional mixing using static or dynamic mixers in addition to other preparation steps. At various stages in such a conventional system, as the emulsion is prepared, the emulsion is first mixed and then pours out of pipes directly into tanks. U.S. Pat. No. 5,000,872 to Olah illustrates such a conventional system in which, for example, the emulsion travels through a static mixer just before pouring into a final emulsion tank at the entry to the transport pipeline. In such a system an opportunity for producing droplets of a uniform size without the need for additional mixers is lost.

Heavy crude emulsions, as well as methods of making such emulsions are disclosed in U.S. Pat. No. 4,618,348 to Hayes et al.; U.S. Pat. No. 4,781,207 to Balzer et al.; U.S. Pat. No. 4,265,264 to Sifferman; and European Patent No. 0 156 486 A2 to Chirinos et al. The emulsifiers utilized in the prior art are numerous. The emulsions in the prior art are manufactured using a variety of mixing conditions and techniques. However, the emulsions of the prior art are difficult to break down into water and oil. Furthermore, the emulsions of the prior art have not been optimized for viscosity and stability to effect efficient transport of these emulsions through pipelines and ultimate utilization.

It has now been found that certain combinations of anionic, nonionic and/or amphoteric emulsifiers, optionally in combination with natural and/or synthetic stabilizers, such as gum, gelatins, carboxymethylcellulose, and the like, when blended at certain shear rates with heavy crude, fuel oil, or the product bottoms from oil barrels, provide an improvement over prior art emulsions. Preparing the emulsions under optimum mixing conditions further enhances their properties. The resulting emulsions form reduced viscosity fluids of controlled stability which fluids can be transported with less effort and which can be utilized more efficiently at the desired destination.

In addition, according to this invention, a diffuser is attached to the end of pipes through which the emulsion must flow to enter an emulsion tank. As the output of the diffuser sprays into the tank droplets of a more uniform and, if desired smaller, size than produced by conventional systems are formed.

SUMMARY OF THE INVENTION

The present invention provides a relatively low viscosity, stable emulsion of heavy, crude hydrocarbons in water, as well as a method for making this emulsion. The heavy crude hydrocarbons are emulsified under shearing conditions and can be heavy crude oil such as Colombian Castilla or Ruhiales crude oil, fuel oil with a viscosity of about 50 to about 2,200 Saybolt Furol Seconds (SSF) at 122° F., the product bottoms from oil barrels, paraffinic crudes, direct water-in-oil emulsions, and the like.

An oil-in-water emulsion embodying the present invention is prepared under controlled fluid dynamic parameters and contains approximately 60% to 85%, preferably 70% to 85% by volume of heavy, viscous crude dispersed in approximately 40% to 15%, preferably 30% to 15%, by volume of an aqueous solution of emulsifiers and, optionally, other additives. The emulsion has a substantially uniform particle size, preferably having a sigma (σ) value of less than about 1.25, and requires less energy for pumping.

The crude oil or heavy crude hydrocarbons can contain relatively large amounts of asphaltenes and metals, and has a specific gravity usually in the range of about 5° API (0.108 Kg/l) to about 30° API (0.676 Kg/l). The emulsifiers can be anionic, nonionic, amphoteric, as well as mixtures thereof. These emulsifiers are present in the produced emulsion at a concentration in the range of about 200 ppm to about 10,000 ppm.

The emulsifiers suitable for making the present emulsion can be anionic emulsifiers such as the sodium alkyl benzene sulfonates, the alkyl sulfonates, the alkyl sulfates, sodium dioctyl sulfosuccinate, and the like. Nonionic emulsifiers such as alkylaryl polyether alcohols, either alone or in combination with the anionic emulsifiers disclosed hereinabove also provide emulsions with the desired properties. Nonionic emulsifiers, if present, are present in an amount of

about 0.05% (500 ppm) to about 0.5% (5000 ppm) by volume. Illustrative amphoteric emulsifiers suitable for present purposes are polyethoxyline amine and oxyethylated sodium salts.

A stabilizing agent can optionally be incorporated into the emulsion, especially if the emulsion is to be stored for an extended period of time and/or transported relatively long distances. The stabilizer can be of either natural or synthetic origin. Examples of suitable stabilizers are gums, gelatins and synthetic hydrophilic polymers such as the water-soluble anionic linear polymers, e.g., sodium carboxymethylcellulose.

The salinity of the crude hydrocarbons to be emulsified, and thus of the resulting emulsion, can be as high as 50,000 ppm of sodium chloride (NaCl) at a temperature in the range of about 10° C. (50° F.) to about 60° C. (176° F.). The pH of the emulsion has a value in the range of about 4 to about 13, and is adjusted to this range by the addition of an aqueous solution of an alkali metal hydroxide such as KOH, NaOH and the like, or an alkaline earth metal hydroxide such as Ca(OH)₂. Buffering compositions can also be utilized for this purpose in order to enhance the long-term storage stability of the present emulsions.

The method for making the present emulsions requires combining the heavy viscous hydrocarbon, which may contain some water, with water, emulsifier and, optionally, a stabilizing and/or an alkalinity agent at a stirring speed of about 50 rpm to about 2000 rpm, preferably at a speed in the range of about 400 to about 800 rpm. These mixing speeds correspond to shear rates of about 0.1 sec⁻¹ to about 20 sec⁻¹ at a power input of about 0.1 hp to about 0.75 hp, preferably about 0.1 hp to about 0.5 hp, for every 1000 barrels (1 barrel=42 std. U.S. gallons) of emulsion. At this shear rate and power input per unit volume an oil droplet size of no more than about 40 μm in at least about 95% of the emulsion volume can be obtained as the agitation is continued.

The method of this invention can be practiced in batch, semi-batch or continuous manner, and is performed by adding small amounts of an emulsifier or group of emulsifiers, with or without an alkalinity agent, to heavy crude oil or other heavy hydrocarbons to be emulsified. The added emulsifiers amount to about 200 ppm by volume to about 10,000 ppm by volume of the emulsion. A stabilizing agent can also be added. Also, emulsions embodying the invention disclosed herein can be prepared from other, previously prepared viscous water-in-oil emulsions. When emulsifiers are added to both the oil phase as well as the aqueous phase, the emulsifiers can be the same or different depending upon the properties of the oil and the desired emulsion. To disperse the oil (the dispersed phase) in the continuous phase (water and emulsifiers, plus, optionally, other ingredients) a mixer adequate to generate a mean droplet size no greater than about 30 μm and a droplet size of no more than about 40 μm in at least about 95% of the emulsion, based on volume, preferred.

Another embodiment of this invention employs a diffuser at the end of pipes which feed into emulsion tanks. This diffuser causes the droplets in the emulsion to elongate in such a way that droplets of uniform size are formed in the tank.

One object of this invention is to provide a method for the preparation of an oil-in-water emulsion having the steps of: (1) combining about 60% to about 85% by volume of a hydrocarbon having a specific gravity of about 5° to about 30° API (American Petroleum Institute standard), in about 15% to about 40% by volume of an aqueous solution to form

an aqueous hydrocarbon mixture, the aqueous solution comprising water and an emulsifier having a hydrophilic-lipophilic balance (HLB) value of about 13.5 to about 16, the emulsifier comprising an anionic emulsifier and a non-ionic emulsifier; and (2) dispersing the hydrocarbon in the aqueous solution of the aqueous hydrocarbon mixture using agitation at a rate of speed of about 50 to about 2000 revolutions per minute and a shear rate of about 0.1 to about 20 second⁻¹ at a power input of about 0.1 to about 0.75 horsepower per 1,000 barrels of the aqueous hydrocarbon mixture for a period of time sufficient to produce an oil-in-water emulsion having a viscosity in the range of 5 to 50 centipoise at 38° C. (100° F.) and stable uniform droplet sizes in the range of 15 to 40 micrometers. Also, this invention includes one or more of the following steps: (1) mixing about 80% to about 99% heavy crude oil or residuals in a temperature range of 100 degrees and 335 degrees Fahrenheit, and about 20% to about 1% of lighter crude oil or diluent (such as a light crude oil having a specific gravity of 18.5 degrees API (American Petroleum Institute standard)) to form the hydrocarbon having a viscosity of about 200,000 centipoise; (2) diffusing the hydrocarbon into the aqueous solution; and/or (3) adding stabilizers to maintain a pH value in the range of about 4 to about 13, the stabilizer selected from the group consisting of: alkali metal hydroxide, hydrochloric acid and alkaline earth metal hydroxide. Furthermore, the agitating step can be continued until at least 95% by volume of the oil-in-water emulsion has an oil droplet size of no more than 40 micrometers and the agitating step can be performed on line using static mixers and/or with a blade-type impeller.

In addition, this invention provides the anionic emulsifier having a concentration of about 200 to about 10,000 parts per million by volume of the oil-in-water emulsion and/or the non-ionic emulsifier having a concentration of about 500 to about 5,000 parts per million by volume of the oil-in-water emulsion. Also, this invention provides that the emulsifier is: (1) nonylphenol ethoxylate having a hydrophilic-lipophilic balance (HLB) value of about 16 and comprising 20 ethylene oxide units per molecule; (2) octylphenol ethoxylate having a hydrophilic-lipophilic balance (HLB) value greater than 13.5; (3) nonylphenol ethoxylate having a hydrophilic-lipophilic balance (HLB) value greater than 13; and/or (4) dioctyl sulfosuccinate having a hydrophilic-lipophilic balance (HLB) value greater than about 13. Also, this invention provides that the aqueous solution includes a stabilizing agent. In addition, this invention provides the diffusing step performed with an atomizer device driven by air impulses.

Another object of this invention is to provide an emulsion having: (1) about 60% to about 85% by volume of a crude oil having a specific gravity from about 5 degrees to about 30 degrees API (American Petroleum Institute standard); and (2) about 40% to about 15% by volume of an aqueous solution comprising water and an emulsifier having a hydrophilic-lipophilic balance (HLB) value of about 13.5 to about 16, the emulsifier comprising anionic and non-ionic emulsifiers having a concentration from about 200 to about 10,000 parts per million by volume of the oil-in-water emulsion, such that the viscosity is in the range from about 5 to 350 centipoise at a temperature of 100 degrees Fahrenheit; and wherein the droplet size is substantially uniform and is no greater than about 40 micrometers. Further, this invention provides for the non-ionic emulsifier having a concentration from about 500 to 5,000 parts per million and/or the anionic emulsifier having a concentration from about 200 to 10,000 parts per million. Also, this invention

provides the emulsion including a stabilizing agent. In addition, this invention provides the emulsion having: (1) a dynamic viscosity at ambient temperature of no more than about 50 Pa.s; and/or a particle size distribution having a sigma value of less than about 1.1.

A further object of the invention is to provide a method of producing energy having the step of combusting an emulsion having about 60% to about 85% by volume of a crude oil having a specific gravity from about 5 degrees to about 30 degrees API (American Petroleum Institute standard); and about 40% to about 15% by volume of an aqueous solution comprising water and an emulsifier having a hydrophilic-lipophilic balance (HLB) value of about 13.5 to about 16, the emulsifier comprising an anionic emulsifier and a non-ionic emulsifier and having a concentration from about 200 to about 10,000 parts per million by volume of the oil-in-water emulsion; such that the viscosity is in the range from about 5 to 350 centipoise at a temperature of 100 degrees Fahrenheit; and wherein the droplet size is substantially uniform and is no greater than about 40 micrometers.

A further object of this invention is to provide a device for forming crude oil droplets of substantially uniform size in an emulsion having: (1) an inlet having at least one receiving passage connected to an end of a pipe; (2) a main body connected to the receiving passage for receiving crude oil from the pipe; and (3) a terminator connected to the main body having at least one exit passage, such that oil droplets are elongated by the exit passages so as to form droplets of the substantially uniform size in the emulsion. This invention also provides the main body including a chamber having at least one sidewall passage, such that elongated droplets form by flowing into the chamber through the sidewall passages and out of the exit passage. Also, this invention provides the main body having a cone shape; and the terminator forming a disk at the large end of the cone shape.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings,

FIG. 1 is a graph showing the effect of temperature on the viscosity of heavy, viscous, dehydrated and non-dehydrated crude oil as well as fuel oil;

FIG. 2, illustrates the effect of different emulsifiers on viscosity and stability of heavy crude oil-in-water emulsions;

FIG. 3 illustrates the effect of emulsifier concentration on viscosity of heavy crude-oil-in-water emulsions;

FIG. 4 illustrates the effect of emulsifier concentration on droplet size and droplet size distribution of heavy crude oil-in-water emulsions;

FIG. 5 illustrates the effect of different types of emulsifiers on droplet size and droplet size distribution in heavy crude oil-in-water emulsion;

FIG. 6 illustrates the effect of oil phase concentration on the viscosity of an oil-in-water emulsion at different emulsifier concentrations;

FIG. 7 illustrates the effect of emulsifier concentration on the viscosity of an oil-in-water emulsion at various oil concentrations;

FIG. 8 illustrates the effect of mixing speed on the viscosity of oil-in-water emulsions with different oil/water ratios;

FIG. 9 illustrates the effect of emulsifier concentration on the viscosity of emulsions using various mixers and various mixing speeds;

FIG. 10 illustrates the effect of mixing time on the viscosity of oil-in-water emulsions using various emulsifiers;

FIG. 11 illustrates the effect of mixing speed on the viscosity of oil-in-water emulsions using various emulsifiers;

FIG. 12 illustrates the effect of mixing speed on the viscosity of oil-in-water emulsions at various emulsifier concentrations;

FIG. 13 illustrates the effect of mixing speed on oil droplet size and droplet size distribution in an oil-in-water emulsion;

FIG. 14 illustrates the effect of the impeller diameter to tank diameter ratio on the viscosity of emulsions with different emulsifiers;

FIG. 15 illustrates the effect of the ratio of impeller diameter to tank diameter on viscosity at different mixing times;

FIG. 16 illustrates the effect of mixing time of droplet size and droplet size distribution;

FIG. 17 illustrates the effect of temperature on emulsion stability;

FIG. 18 illustrates the effect of pH on emulsion stability over time;

FIG. 19 illustrates the Theological behavior of the emulsion calculated from pilot plant flow data as compared to direct measurements using a concentric viscometer;

FIG. 20 illustrates the effect of pumping time on droplet size and droplet size distribution;

FIG. 21 is a photomicrograph of an oil-in-water emulsion made according to the present invention at 300x magnification;

FIG. 22 is a photomicrograph of another emulsion made according to the present invention at 160x magnification;

FIG. 23 is a graphical representation of the particle sizes and particle size distributions of the emulsions shown in FIGS. 21 and 22;

FIG. 24 is a cross-sectional view of a nozzle system diffuser according to one embodiment of the subject invention; and

FIG. 25 is a cross-sectional view of a cone-type diffuser according to one embodiment of the subject invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Readily pumpable heavy crude oil-in-water emulsions of relatively low viscosity can be prepared under controlled shearing conditions using a variety of emulsifiers having a Hydrophilic-Lipophilic Balance (HLB) value in the range of about 13.5 to about 16.

Emulsifiers can be used either singly or in combination with other emulsifiers of the same family, although having a different HLB value or a mixture of two or more emulsifiers of different compatible families, as long as the HLB value of the combination remains within the aforesaid range. The HLB value of an emulsifier quantifies the relative simultaneous attraction thereof for water and oil. It is determined by the chemical composition of the emulsifier and the extent of its ionization. For example, ionic emulsifiers change HLB values radically with a change in pH and/or salt content of an emulsion, whereas non-ionic emulsifiers exhibit a more nearly constant HLB under such circumstances. The emulsifier for practicing the present invention can be either anionic, nonionic, amphoteric or mixtures thereof.

The optimum, and thus preferred, emulsifiers for the emulsions contemplated by the present invention are those which provide optimum viscosity, stability and interfacial tension to the emulsion. The emulsifier is mixed with water. Oil is then combined with the resulting mixture. The optimization of the present emulsions can be carried out using water with a salinity of up to 50,000 ppm and at a temperature of about 10° C. (50° F.) to about 95° C. (200° F.), depending upon the nature of the heavy hydrocarbon to be emulsified and its water content. For a relatively more viscous hydrocarbon the emulsification is effected at a relatively higher temperature. At temperatures lower than 10° C., emulsions of paraffinic crude may produce paraffin crystals which precipitate from the emulsion. This phenomena can be minimized, if desired, by the addition of a pour point depressant to the hydrocarbon prior to emulsification.

Illustrative anionic emulsifiers that impart optimum properties to the emulsion are, for example, the sodium alkyl benzene sulfonates with a molecular weight of about 350 to about 665, the alkyl sulfonates, the alkyl sulfates, and sodium dioctyl sulfosuccinate in an amount in the range of about 200 ppm by volume (0.02 vol. %) to about 10,000 ppm by volume (1 vol. %) of the total emulsion volume. A suitable emulsifier can also be produced by sulfonating fatty acids derived from coffee beans. Typical such fatty acids are constituted primarily by palmitic acid and linoleic acid. An illustrative composition of fatty acids derived from coffee beans that can be sulfonated to produce a suitable emulsifier is as follows:

palmitic acid	about 36.4 wt. %
stearic acid	about 7.1 wt. %
oleic acid	about 7.3 wt. %
linoleic acid	about 41.3 wt. %
linolenic acid	about 1.3 wt. %
arachidic acid	about 2.5 wt. %

Nonionic emulsifiers such as alkyl aryl polyether alcohols were also found suitable for the emulsions disclosed herein. Such emulsifiers are prepared by reaction of octylphenol or nonylphenol with ethylene oxide. The nonionic emulsifiers can be utilized in an amount of about 500 ppm by volume (0.05 vol. %) to about 5000 ppm by volume (0.5 vol. %) of the total emulsion volume.

A mixture of the anionic emulsifiers and nonionic emulsifiers is also contemplated as useful in the present emulsions. The mixture of anionic and nonionic emulsifiers exhibits greater salinity tolerance, which is useful if the water used to prepare the emulsion has a significant saline concentration. The respective weight ratios of anionic-to-nonionic emulsifiers in such mixtures can be in the range of about 30:70 to about 80:20. This weight ratio can be readily optimized for a particular crude by routine experimentation.

Amphoteric emulsifiers such as the polyethyline amines, oxyethylated sodium salts containing both anionic and cationic centers, and the like, are also suitable for the practicing of this invention.

A stabilizing agent can be combined with the emulsifier to stabilize the emulsion. The stabilizer can be of natural or synthetic origin.

The stabilizers of natural origin are exemplified by water-soluble gums, i.e., complex carbohydrates that yield sugars on hydrolysis, such as gum arabic, the carrageenans, locust bean gum, and the like. Particularly preferred are the arabian type gums such as gum arabic (derived from *Acacia senegal*), and the like. Also suitable are gum ghatti (derived

from *Anogeissus latifolia*), gum karaya (derived from *Sterculia urens*), and the like.

The stabilizers of synthetic origin can be natural based such as the water-soluble anionic linear polymers exemplified by sodium carboxymethylcellulose, or petroleum-based such as the polymerized vinyl-type monomers modified to contain acidic function and exemplified by polyacrylic acid and the derivatives thereof, e.g., polyacrylic acid polymers lightly cross-linked with a polyalkenyl polyether and commercially available under the designation CARBOPOL™. Also suitable are the polyvinylpyrrolidones, carboxyvinyl polymers, and mixtures of the foregoing.

The emulsions herein described can be prepared using either heavy crude oils, the bottom product from oil barrels, paraffin crudes and medium and light crude oils. Heavy crudes such as the Colombia Castilla or the Rubiales crude oil, and fuel oils with a viscosity of about 50 to about 2200 SSF (122° F.), when emulsified according to this invention, are transported and utilized with greater efficiency. The disclosed method is particularly effective for preparing a High Internal Phase Ratio (HIPR) emulsion using heavy, viscous crudes that potentially contain large amounts of asphaltenes and metals with a specific gravity (60/60) between about 5° API (0.108 Kg/l) and 30° API (0.676 Kg/l). If desired, the heavy crude can be diluted with a lighter hydrocarbon, e.g., light cycle oil (about 18.5° API) to a viscosity of about 200,000 cPs (200 Pa.S) prior to emulsification.

In order to properly assess the process disclosed herein, emulsions were prepared using medium crudes (22°–30° API), heavy crudes (14°–21° API) and extra heavy crudes with an API density less than 14° API. The heavy crudes comprise 60% to 85% by volume of the emulsion, preferably 70% to 85% by volume.

Emulsions with a higher oil content are more economical to transport because more oil is transferred per unit volume of emulsion. The viscosity of the emulsion increases with higher crude oil content, however, and losses due to increased viscosity preclude increasing the oil content of the emulsion above a certain level.

Work is required to disperse the oil droplets in the continuous (aqueous) phase. By breaking the dispersed phase into droplets, more surface area of the dispersed phase is exposed to the continuous phase. The type of mixing equipment used also affects the nature of the produced emulsion. The degree or time of agitation, the type stirrer, the speed or the shear rate, and also the process type (i.e., batch, semibatch or continuous) and whether the process is static or dynamic, influences the type of emulsion that results. Generally a suitable mixer is one that effectively disperses a high viscosity fluid (heavy crude) in a lower viscosity solution (water plus emulsifier and other ingredients).

Impellers of the blade-type are suited for use in conjunction with the mixing equipment used to effect the desired dispersion of the oil phase into the aqueous phase. Flat blade, disc flat blade, curved blade and pitched blade impellers all perform effectively at a rotational speed of about 50 to about 2000 rpm. This is equivalent to a shear rate of about 0.1 sec⁻¹ to about 20 sec⁻¹ at a power input of about 0.1 hp to about 0.75 hp, preferably about 0.1 hp to about 0.5 hp, per 1000 barrels of the emulsion. Forty-two standard U.S. gallons equal one barrel. The preferred impellers are those that have a relatively high discharge capacity with a relatively low head when used with a mixture that is about 60% to 85% by volume heavy, viscous hydrocarbon and about 30%

to 15 volume percent water and other additives at a stirring speed of 50 to 200 rpm, preferably 400 to 800 rpm.

The impeller diameter-to-tank diameter ratio also impacts the emulsion properties. A ratio of about 0.5 to about 0.4 for impeller diameter-to-tank diameters is preferred. The ratio of liquid column height to tank diameter can also impact emulsion properties. A column height-to-tank diameter ratio of about 0.9 to about 0.5 is preferred.

The selected emulsifiers are combined with water and the resulting aqueous admixture amounts to 15% to 40%, preferably 15% to 30%, of the total emulsion volume. The crude oil is then mixed with the aqueous admixture using an agitator as described herein, preferably at about 400 to 800 rpm. Alternatively, emulsification can be achieved using a static mixer or an air-driven atomizer.

The heavy, viscous crude oil is dispersed in the admixture of water and emulsifier at a temperature of about 4° C. (40° F.) to about 82° C. (180° F.), preferably at a temperature of about 50° C. (122° F.) to about 60° C. (140° F.).

Higher temperatures and pressures, e.g., 100° C. (212° F.) to about 168° C. (335° F.) at superatmospheric pressures up to about 200 psia, can be utilized as well during emulsification.

The water may be fresh or saline water with a salt concentration of up to about 50,000 ppm by volume. The dynamic viscosity of the produced emulsions is about 5 cPs (0.005 Pa.S) to about 350 cPs (0.35 Pa.S) at 38° C. (100° F.), preferably about 5 cPs to about 50 cPs (0.05 Pa.S), depending upon the starting materials. (1 cP=0.001 Pa.S=1 mPa.s)

The emulsions described herein can also be prepared starting with a water-in-oil emulsion having a dynamic viscosity of about 2,000 cPs (2 Pa.S) to about 300,000 cPs (300 Pa.S). The water-in-oil emulsion contains about 5% to about 20% volume percent water. The emulsifier and additional water are added to the water-in-oil emulsion in amounts sufficient to produce the oil-in-water emulsion herein described.

The pH of the emulsion may vary from about 4 to about 13. Alkaline solutions of hydroxides of alkali metals, e.g. potassium and sodium, or an alkaline earth metal such as calcium, can be added to the emulsion to adjust the pH to within this range if necessary. Similarly, hydrochloric acid can be added to lower the pH to a value within the above range, if necessary. The saline concentration of the emulsifier solution preferably is no more than about 50 ppm, by weight, but can be as high as 50,000 ppm.

When a paraffinic crude with a relatively high pour point of about 15.5°–26.7° C. (60°–80° F.) is emulsified in accordance with the process disclosed herein, the pour point is lowered. This provides an improved flow of the crude at relatively lower temperatures when the crude is emulsified according to the disclosed process. The paraffinic crudes exhibit a relatively lower viscosity when emulsified according to the disclosed process. A pour point modifier can be added to the emulsion to raise or lower the pour point, if desired. Suitable pour point modifiers are ethylene interpolymers, ethylene-vinyl acetate copolymers, polyacrylate copolymers, and the like, in an aromatic liquid vehicle such as the xylenes, toluene, and the like.

The flow characteristics of the produced emulsion also depend on whether this emulsion is a Newtonian or non-Newtonian fluid. An emulsion that exhibits Newtonian behavior is preferred because Newtonian fluids maintain a constant viscosity over a broad range of shear rates and, thus are more stable under different flow conditions. In non-Newtonian fluids, on the other hand, viscosity varies with

the shear rate and non-Newtonian emulsions are less stable under different flow conditions.

The shearing conditions contemplated by the present method as disclosed herein minimize the interfacial tension between the oil and water phases in the emulsion. This, in turn, minimizes the viscosity of the emulsion, thereby enhancing its flow characteristics and reducing power requirements for pumping. The lower the interfacial tension, the lower the droplet-to-droplet interaction. This is so because the droplets elongate more easily along stream-flow lines rather than colliding with one another and creating resistance to flow. Because of the low interfacial tension and low viscosity of the emulsion, a relatively narrower droplet size distribution is achieved. Thus, the mean droplet size can be more easily regulated. A mean droplet size of less than about 30 μ m provides the desired Newtonian flow characteristics to this emulsion. Preferably, the mean droplets size is less than about 20 μ m, oil droplets about 40 μ m or less in diameter are present in at least about 95% of the emulsion disclosed herein. The desired droplet size can be achieved by optimizing the fluid-mechanical parameters such as agitator speed, agitation time, agitator type, etc. as disclosed herein. The sigma (σ) value of the present emulsions, a measure of particle size distribution, preferably is less than about 1.25, more preferably no more than about 1.1.

The emulsion disclosed herein also exhibits improved pumpability, combustion characteristics and dehydration properties over heavy, viscous hydrocarbon oil-in-water emulsions in the prior art. The emulsifiers used in the formulation have optimum affinity for the aqueous phase, thereby imparting improved properties to the emulsion. The heating value of the present emulsions preferably is at least about 13,000 BTU/pound.

Maximizing the solubility of oil and water into one another by using the proper emulsifier produces an emulsion with the desired properties. Furthermore, by adjusting the emulsifier composition, one can tailor an emulsion for particular use; highly stable emulsions if they will be stored in tankers for a great length of time; emulsions that are easily resolved into their components if the end use so dictates; and emulsions that can be directly combusted if phase separation is not required.

The emulsions prepared according to the above-described process usually exhibit a pH value in the range of about 4 to about 13. Emulsions exhibiting a pH value of about 7 to about 10 are more stable, but can be readily broken down, i.e. separated into oil and water components, when desired, by acidification to a pH value of less than about 7, usually a pH value in the range of about 4 up to 7. A deemulsifying agent such as polyethoxyalkylamine can also be used for this purpose. The heavy crude separated from the emulsion has a water content of about 0.5% by volume. The water separated from the crude usually contains approximately 0.001% to about 0.003% (10–30 ppm) by volume of heavy crude oil, but can contain up to about 0.005% (50 ppm) by volume of heavy crude oil.

The emulsions disclosed herein can be broken down and the dispersed and continuous phases thereof separated using a chemical method in which the pH of the emulsion is changed from basic to acidic or vice-versa depending upon its initial pH. Surface active agents that modify the hydrophilic nature of the emulsifier system that is present are also useful to break down these emulsions. Neutralization of the hydrophilic forces, or their eliminations, eliminates the major forces that keep the emulsions stable. Thus, the emulsions are easier to break down. With the emulsifiers

used herein, the separation of the oil and water phases of the emulsion is readily achieved by lowering the pH value of the emulsion.

The following examples are evaluations of the emulsions disclosed herein and made according to the method of this invention. Various properties of emulsions made with different emulsifiers at different concentrations and different oil-to-water ratios were evaluated to determine the optimum emulsion properties for the various contemplated applications. The effect of different mixing or stirring parameters was evaluated to determine the optimum conditions needed to prepare the desired emulsions. These examples are made by way of illustration only to highlight the more general discussion of the inventive concepts disclosed hereinabove and the claims appended hereto.

Several viscous crude oils were used to evaluate the efficacy of the process disclosed herein. The crudes used were obtained from the oil fields of Colombia, which yield some of the most viscous, difficult-to-transport crudes similar to the Venezuelan and Canadian crudes. A summary of the characteristics of the crude oil used in these examples is found in Table I hereinbelow. The properties of the crude oils evaluated in Table I were determined using ASTM Standards D-97, D-287, D-96 and D-3230-13.

TABLE A

Colombian Castilla Heavy Crude Oil Characteristics		
Characteristic	Non-Dehydrated Crude Oil (BS&W = 15.6%)	Dehydrated Crude Oil (BS&W = 0.5%)
API Density (60° F.)	12.6	13
Specific Gravity (60/60)	0.982	0.9792
Density (Kg/l) @ 15° C.)	0.9814	0.9787
Pour Point (°C.)	4° C.	0.3° C.
Salinity (PTB)	100	—
Viscosity (cP) @ (25° C.)	15,189	7,530
Viscosity (cP) @ (55° C.)	1,195	408

BS&W = basic sediment and water

EXAMPLE 1

Effect of Temperature on Emulsion Viscosity

The viscosity of the crude oils used in the present examples was determined using CV100 and RV20 Haake concentric viscometers at different temperatures, and recorded. The data are presented in FIG. 1. As can be observed from FIG. 1, the viscosity of the crude is dramatically reduced by an increase in the temperature. The effect of temperatures on the crude oil viscosity is slightly more pronounced when the crude is hydrated.

EXAMPLE 2

Effect of Different Emulsifiers on Emulsions

Several emulsions were prepared using different emulsifiers. Emulsifiers with HLB values of about 13.5 to about 16 were utilized in these emulsions. These emulsions were prepared by adding the viscous hydrocarbon to water and emulsifier combination. The mixtures were all agitated mechanically at a speed of 600 rpm. The resulting emulsions were 75% by volume oil and 25% by volume water.

FIG. 2 and FIG. 3 illustrate the properties of the emulsions that were prepared using emulsifiers of various HLB values. The emulsions formed had relatively good stability. An emulsion exhibits good stability by remaining in its emul-

sified state, rather than the dispersed and continuous phase separating completely. The emulsion with a mixture of an anionic emulsifier, sodium sulfosuccinate, and nonionic emulsifier, nonylphenol ethoxylate, (HLB>13) exhibited the greatest stability of the emulsions tested. FIG. 2 illustrates the stability of the emulsions of the oil-in-water emulsions as indicated by the amount of water that separate from the emulsions after 120 hours at a temperature of 80° C. (176° F.). The emulsifiers used in these emulsions are enumerated in the Table II below.

TABLE II

Emulsifiers Tested			
N	Family	Emulsifier	HLB
1	Nonionic	Nonylphenol ethoxylate	16
2	Anionic + Nonionic	A 30 wt % Anionic/70 Wt % Nonionic Mixture	>13
3	Anionic	Diocetyl sulfosuccinate	>13
4	Nonionic	Nonylphenol ethoxylate	13.5
5	Nonionic	Octylphenol ethoxylate	13.5

Nonionic surfactants with HLB values of 13.5 produced the least stable emulsions while the emulsion formed with the anionic/nonionic emulsifier mixture had a relatively greater stability.

FIG. 3 illustrates the effect of the various emulsifiers from Table II on the viscosity of the emulsions prepared therewith. As is apparent from FIG. 3, most of the viscosity reduction is achieved at emulsifier concentrations of about 550 ppm to 1500 ppm by volume, regardless of the emulsifier used. The emulsifiers tested were those enumerated in Table II above.

At emulsifier concentrations in excess of 2000 ppm, the reduction in viscosity that is obtained is seldom justified by the additional expense of the increased amount of emulsifier used. Furthermore, the fluid dynamics of the agitation provide stability to the emulsion, thereby reducing the need for larger amount of emulsifiers.

EXAMPLE 3

Effect of Emulsifier Concentration on the Emulsion Droplet Size

Emulsions were prepared that contained crude oil (70% by volume), water, and emulsifier. The emulsion temperature was 25° C. (77° F.). An anionic emulsifier, dioctyl sulfosuccinate, was utilized in the emulsions. Two emulsions were prepared of similar composition; one with an emulsifier concentration of 500 ppm (by volume) and one with a concentration of 1,000 ppm (by volume). FIG. 4 illustrates the effect of emulsifier concentration on droplet size distribution. An emulsifier concentration of 0.1% by volume (1000 ppm) yielded a preferred mean droplet size of less than about 30 μm.

Heavy crude oil-in-water emulsions were prepared with 70% heavy crude and various emulsifiers, all with an HLB greater than 13 at a concentration of 0.08% (800 ppm) by volume. The mean oil droplet size of the emulsions was determined. FIG. 5 illustrates that all of the emulsifiers provide an acceptable mean droplet size of about 30 μm or less to the emulsion. The emulsifiers tested were Emulsifiers 1-3 from Table II above. An emulsifier that is a mixture of anionic and nonionic emulsifiers yielded a preferred droplet size of about 10 μm with a narrower range of droplet size distribution.

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EXAMPLE 4

Effect of Oil Phase Concentration on Emulsion Viscosity

Emulsions were prepared according to the process disclosed herein using a nonionic, nonylethoxylate type emulsifier with an HLB of 16. There were approximately 20 ethylene oxide units per molecule in the emulsifier. The percent of heavy, viscous crude oil in the emulsion was varied at different emulsifier concentrations. The crude oil used in the emulsions had a viscosity of 15,500 cPs (15.5 Pa.S). A propeller type agitator at a speed of 600 rpm was used to stir the emulsion. The observed viscosities are presented in FIG. 6 which illustrates that the viscosity of the emulsions is very low when the percentage of viscous crude oil in the emulsion is below about 75% by volume, regardless of emulsifier concentration, at an emulsifier temperature of 25° C. (77° F.).

The data from the same experiments and presented in FIG. 7 illustrate that emulsifier concentrations greater than 3000 ppm by volume do not further reduce the emulsion viscosity to a significant extent regardless of the volume of heavy crude in the emulsion.

EXAMPLE 5

Effect of Stirring Speed on Emulsion

Emulsions of a crude oil with a viscosity of about 15,000 cP to about 100,000 cP and a water solution of a nonylphenol ethoxylate, a nonionic emulsifier (HLB=13.5), were prepared. The stirring speed was varied for emulsions with oil-in-water concentration ratios (O/W) of 75/25, 70/30 and 65/35. The higher water content emulsions had a lower viscosity. For the various concentrations of oil in water, a stirring speed of about 600 rpm produced the emulsions of lowest viscosity. The emulsions made at stirring speeds of greater than 1000 rpm had noticeably higher viscosity. These results are illustrated in FIG. 8.

EXAMPLE 6

Effect of Stirring Parameters on Emulsion Viscosity

Emulsions with an O/W ratio of about 70/30 were prepared using various stirrers with various impellers. The emulsifier used was nonylphenol ethoxylate, a nonionic emulsifier (HLB=13.5). The effect of emulsifier concentration on the viscosity of these emulsions was observed. The results appear in FIG. 9. The percent decrease in viscosity observed when the emulsifier concentration was increased from 500 ppm to 2500 ppm by volume was less than the percent decrease in viscosity observed when the mixer was changed from a helical-type at 600 rpm to a propeller-type impeller at 600 rpm. Thus, at a given emulsifier concentration, the type of impeller used and the speed at which it rotates have a demonstrated effect on the emulsions viscosity.

Furthermore, the differences in viscosity of emulsions prepared using the different type impellers and stirring speeds at a given emulsifier concentration are somewhat uniform over a wide range of viscosities. This indicates that the effect of stirring conditions on the emulsion is somewhat independent of emulsifier concentration.

EXAMPLE 7

Effect of Stirring Time on Emulsion Viscosity

Emulsions were prepared with an O/W ratio of 70/30 by volume at a temperature of 25° C. (77° F.). The emulsifier

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concentration was 0.1% by volume (1000 ppm). Emulsifiers 1-4 from Table II were used to formulate the emulsions, all with HLB values of about 13.5 or greater. The stirring speed was 400 rpm.

FIG. 10 illustrates the effect of stirring time on the viscosity of these emulsions. It appears that stirring time in excess of 10 minutes results in very little additional viscosity reduction. The anionic emulsifiers and the mixtures of anionic and nonionic emulsifiers with relatively high HLB values yielded emulsions with the lowest viscosity regardless of stirring time.

EXAMPLE 8

Effect of Stirring Speed on Emulsion Viscosity

Heavy crude oil-in-water emulsions (70% by volume oil) were prepared. In order to evaluate the effect of stirring speed on viscosity and droplet size distribution, the emulsions were prepared at various mixing speeds and using various kinds of emulsifiers (Emulsifiers 1, 4 and 5 from Table II) at a concentration of 0.1% by volume (1000 ppm).

The obtained data are presented in FIG. 11 and illustrate that a stirring speed of about 600 rpm results in optimum viscosity reduction of the emulsion.

Emulsions were also prepared with a nonylphenol ethoxylate emulsifier (HLB=16) at concentrations of 1000, 2000 and 3,000 ppm by volume. The obtained data are presented in FIG. 12. Again, optimum viscosity reduction was achieved at a stirring speed of about 600 rpm independently of emulsifier concentration.

Only a slight reduction in viscosity was obtained when emulsifier concentrations were increased above 2000 ppm. The increase obtained does not appear to justify the cost of additional emulsifier at current prices.

EXAMPLE 9

Effect of Stirring Speed on Emulsion Oil Droplet Size

An emulsion was prepared that was 70% by volume crude oil. The emulsifier used was a nonionic nonylphenol ethoxylate-type with an HLB value of about 16. The emulsifier concentration was 0.1% (1000 ppm) by volume. The effect of stirring speed on droplet size and distribution is illustrated by the data presented in FIG. 13. The test was conducted at 25° C. (77° F.).

From the data in FIG. 13 it is readily apparent that a stirring speed of 600 rpm yields a more acceptable mean droplet size and distribution than is obtained at either 400 rpm or 1200 rpm. Though the mean droplet size obtained at 1200 rpm was acceptable, the uniformity of the droplet size was not as good as that obtained at 600 rpm.

EXAMPLE 10

Effect of Stirrer Type on Emulsion Properties

The mechanics of stirring has a large impact on the properties of the emulsion produced thereby. Not only do the impeller design and the speed of rotation of the agitator effect the viscosity and oil droplet size of the oil-in-water emulsion, the tank configuration in conjunction with the agitator design is also significant.

Emulsions were prepared that were 70% by volume crude in water. A nonionic emulsifier (HLB=16) was used to make one emulsion at a pH of 10 and an anionic emulsifier was used

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to make another emulsion at a pH of 7. The emulsifier concentrations were 1000 ppm by volume in both instances. Both emulsions were stirred at 600 rpm stirring speed at a temperature of 25° C. (77° F.) under conditions wherein two different ratios of impeller diameter-to-tank diameter were used. When stirred at the higher ratio, both emulsions had a lower viscosity. The observed data are presented in FIG. 14.

A relatively higher impeller diameter-to-tank diameter ratio can also reduce stirring time. The emulsion with the nonionic emulsifier (HLB=16) was stirred under conditions in which two different impeller diameter-to-tank diameter ratios were used. The observations presented in FIG. 15 clearly illustrate that the emulsion stirred using the relatively higher ratio achieved a lower viscosity in less time.

EXAMPLE 11

Effect of Stirring Time on Emulsion Droplet Size

An oil-in-water emulsion was prepared that was 70% by volume crude oil. An anionic emulsifier was present in the emulsion in a concentration of about 1000 ppm by volume. The temperature of the emulsion was 25° C. (77° F.). The emulsion, total volume of 300 liters, was stirred at a speed of 600 rpm using a propeller type mixer. The effect of the stirring time on the mean oil droplet size and droplet size distribution in the emulsion was noted, and is presented in FIG. 16. The data in FIG. 16 shows that the mean droplet size decreases and the droplet size distribution narrows the longer the emulsion is stirred. The droplet size was measured in a Malvern Series 2600c Droplet and Particle Sizer. The mean droplet size refers to the Sauter mean diameter (SMD) thereof, i.e. the diameter of a droplet whose surface-to-volume ratio is equal to the combined surface-to-volume ratio of all of the oil particles in the emulsion.

EXAMPLE 12

Effect of Time and Temperature on Emulsion Stability

Oil-in-water emulsions have to be separated, i.e., broken down, into oil and water phases, depending upon the end use of the emulsion. For example, if the oil in the emulsion is to be refined, the water phase must be separated from the oil phase prior to refining. If the oil is to be direct fired, however, the emulsion does not have to be broken down prior to use. However, the emulsion should not break down over time or during transport. Prior art emulsions are at times difficult to separate or break, primarily because of the small or irregular droplet size of oil in the water. The relatively high surface area-to-volume ratio of the oil droplets makes it more difficult to separate the emulsion. At other times, prior art emulsions break down too easily, and the transport properties of the emulsion, i.e. reduced viscosity, are lost.

FIGS. 17 and 18 present data obtained when the present emulsions (O/W: 70/30) are broken, and illustrate that the emulsions disclosed herein were easily broken by temperature or by adding a chemical additive. FIG. 17 clearly illustrates that phase separation is achieved more quickly at a relatively higher temperature. Similar results have been obtained with O/W: 75/25.

FIG. 18 illustrates the rate at which the emulsion breaks down when no emulsifier is present therein. At a pH of 4.5 more than 90 wt-% of the water had separated from the oil within 20 minutes. The broken emulsion ultimately produced substantially clear water and a substantially water-

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free viscous hydrocarbon with less than 0.5% by volume water therein. A demulsifying agent effected separation of an oil-in-water emulsion with an emulsifier therein at a concentration of 20 ppm by volume, but over a greater period of time. The demulsifying agent used was a nonionic emulsion breaker, alkyl aryl polyether alcohol with an HLB value of 10.

EXAMPLE 13

Effect of Transport on Emulsion Viscosity

The emulsion was evaluated to determine the effect of transportation through a pipeline thereon. The emulsion tested was a 70/30 oil-in-water emulsion made with an anionic, dioctyl sodium sulfosuccinate emulsifier present in a concentration of 1000 ppm (0.1%) by volume. The temperature of the emulsion was 25° C. (77° F.). Pumping the emulsion through the pipeline was accomplished using centrifuges and gear pumps through test loops of pipe that were 36 feet in length and of varying diameters (e.g., 1 inch, ½ inch, ¼ inch, etc.). The emulsion was pumped in the loop from a tank therein for 3 days. FIG. 19 illustrates a proportional relationship between shear stress and shear rate, which is a characteristic of Newtonian behavior.

FIG. 19 also illustrates that the change in shear rate vs. shear stress for the emulsion is similar whether the emulsion rheology is evaluated using flow data from a pilot plant pipeline or from data obtained using a concentric viscometer in the laboratory. This indicates that the viscometer is a fairly accurate representation of actual pumping conditions, and also that the present emulsification process can be scaled up readily. It has also been observed that the emulsion viscosity remained substantially constant as the flow rate was increased.

FIG. 20 presents in graphical form the observed droplet size increase over time during pumping. The droplet size was measured in the same manner as the previous example. While the droplet size increased somewhat, this increase was not significant. The data shown in FIG. 20 demonstrates the overall good stability of the present emulsions.

EXAMPLE 14

Direct Combustion of the Emulsion

Though the emulsion is readily separated into oil and water components, in some instance it is desirable to combust the emulsion without breaking it down. A Castilla heavy crude 75/25 oil-in-water emulsion prepared in accordance with this invention using about 1,000 ppm of sodium alkylbenzene sulfonates was burned in a conventional, induced draft, air cooled combustion chamber equipped for firing diesel fuel at a rate of 1.5 MBtu/h. The O/W emulsion was burned and its combustion was compared to diesel fuel and heavy Castilla crude oil. The viscosity of the three fuels was 90, 12 and 7500 cPs, respectively. The emulsion was ignited readily. There was no appreciable difference in appearance between the emulsion flame and the diesel fuel flame. The flame temperature of the diesel fuel flame was 1000° C. (1832° F.) while the emulsion flame temperature was 900° C. (1652° F.). This however, is not viewed as a disadvantage as relatively lower flame temperatures decrease the formation of nitrogen oxides.

EXAMPLE 15

Emulsion Droplet Size and Droplet Size Distribution

FIG. 21 and FIG. 22 are photomicrographs of emulsions made according to the present process. Specifically, the

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emulsion shown in FIG. 21 (300x) was prepared using a propeller-type agitator (600 RPM; shear rate 10 sec^{-1}) and about 2,000 ppm (by volume) of dioctyl sodium sulfosuccinate as the emulsifier (anionic). The produced oil-in-water emulsion O/W: 65/35 was observed to have a mean droplet size of about $17.9 \mu\text{m}$, a maximum droplet size of about $37.6 \mu\text{m}$, and a minimum droplet size of about $1.9 \mu\text{m}$. Emulsion viscosity was observed to be about 45 cP (25°C .), and the emulsion exhibited a sigma (σ) value of about 1.2.

The illustrative emulsion embodying the present invention and shown in FIG. 22 (160x) was prepared using a propeller-type agitator (600 RPM; shear rate 10 sec^{-1}) and about 1,500 ppm (by volume) of dioctyl sodium sulfosuccinate as the emulsifier (anionic) for the Castilla crude oil. The produced oil-in-water emulsion (O/W: 70/30) was observed to have a mean droplet size of about $17.5 \mu\text{m}$, a maximum droplet size of about $25.6 \mu\text{m}$, and a minimum droplet size of about $1.9 \mu\text{m}$. Emulsion viscosity was observed to be about 50 cP (25°C .), and the emulsion exhibited a sigma (σ) value of about 1.1.

The substantially uniform droplet size as well as the droplet size distribution of the emulsions shown in FIGS. 21 and 22 can be readily seen from the graph presented as FIG. 23.

FIG. 24 is a cross-section illustration of a device according to one embodiment of this invention for producing the droplets having substantially uniform size, that is, atomizing the heavy crude oil or emulsion. This embodiment employs a nozzle system 100 as part of the emulsion production. In operation, crude oil 102, or emulsions thereof, travels down a pipe 104 into a nozzle attachment 106 which is attached at the end of the pipe 104. The nozzle attachment 106 contains a cylindrical guard 108 with an outer sleeve 110 at one end for termination and to form a chamber 112. The guard 108 forms the main part of the chamber 112 and the end of the chamber 112 is formed by a nozzle cap 114 which has a decreasing internal radius from one end toward the other end which includes an exit port 116. An increasing internal radius is formed after the exit port 116. The crude oil 102 flows into the chamber through passages 118 formed in the sidewall 120 of the guard 108. This nozzle system 100 causes the crude oil 102 to be emitted from the exit port 116 as a fan spray 122 of droplets, the droplets having substantially uniform size. The flow of the crude oil 102 through the passages 118 and out through exit port 116 causes the droplets to elongate in such a way that forces of cohesion and adhesion produce droplets of substantially uniform size in the tank into which the droplets are sprayed. Although the diffuser is discussed above as diffusing crude oil, the diffuser of this invention is also used with various mixtures and emulsions including heavy crude and/or other types of oil. Thus, for example, references to crude oil should be read to include emulsions containing crude oil.

Although the nozzle system discussed above employs a nozzle, other types of spray producing atomizers can be used. For example, in one embodiment a diffuser 130 is shaped like a shower attachment, see FIG. 25. In this example, instead of a nozzle system, the narrow end 132 of the cone-shaped diffuser 130 is attached to the end of a pipe 133. The other, larger end of the diffuser is terminated by disk 134 having multiple holes 136, each hole having a radius sufficient for elongating the droplets such that after ejection through the holes into the tank, the droplets have substantially uniform size.

The examples enumerated hereinabove and the accompanying discussion are intended to illustrate the general prin-

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ciples that are applicant's invention. Nothing in the specification or examples is to be construed as a limitation of the invention as defined by the claims.

We claim:

1. A method for the preparation of an oil-in-water emulsion comprising the steps of:

combining about 60% to about 85% by volume of a hydrocarbon having a specific gravity of about 5 degrees to about 30 degrees API, in about 15% to about 40% by volume of an aqueous solution to form an aqueous hydrocarbon mixture, the aqueous solution comprising water and an emulsifier having a hydrophilic-lipophilic balance (HLB) value of about 13.5 to about 16, the emulsifier comprising an anionic emulsifier and a non-ionic emulsifier; and

dispersing the hydrocarbon in the aqueous solution of the aqueous hydrocarbon mixture using agitation at a rate of speed of about 50 to about 2,000 revolutions per minute and a shear rate of about 0.1 to about 20 second^{-1} at a power input of about 0.1 to about 0.75 horsepower per 1,000 barrels of the aqueous hydrocarbon mixture for a period of time sufficient to produce an oil-in-water emulsion having a viscosity in the range of 5 to 50 centipoise at 38°C . (100°F .) and stable uniform droplet sizes in the range of 15 to 40 micrometers.

2. The method of claim 1, further comprising, before the combining step, the step of:

mixing about 80% to about 99% heavy crude oil or residuals in a temperature range of 100 degrees and 335°F , and about 20% to about 1% of lighter crude oil or diluent to form the hydrocarbon having a viscosity of about 200,000 centipoise.

3. The method of claim 1, wherein the combining step comprises the step of:

diffusing the hydrocarbon into the aqueous solution.

4. The method of claim 1, wherein the agitating step is continued until at least 95% by volume of the oil-in-water emulsion has an oil droplet size of no more than 40 micrometers.

5. The method of claim 1, wherein the agitating step is performed on line using static mixers.

6. The method of claim 1, wherein the anionic emulsifier has a concentration of about 200 to about 10,000 part per million by volume of the oil-in-water emulsion.

7. The method of claim 1, wherein the non-ionic emulsifier has in a concentration of about 500 to about 5,000 parts per million by volume of the oil-in-water emulsion.

8. The method of claim 1, wherein the aqueous solution further comprises a stabilizing agent.

9. The method of claim 1, wherein the emulsifier is selected from the group consisting of:

a nonylphenol ethoxylate having an hydrophilic-lipophilic balance (HLB) value of about 16 and comprising 20 ethylene oxide units per molecule, an octylphenol ethoxylate having an hydrophilic-lipophilic balance (HLB) value greater than 13.5, a nonylphenol ethoxylate having a hydrophilic-lipophilic balance (HLB) value greater than 13, and a dioctyl sulfosuccinate having a hydrophilic-lipophilic balance (HLB) value greater than about 13.

10. The method of claim 1, further comprising one or more steps of:

adding a stabilizer to maintain a pH value in the range of about 4 to about 13, the stabilizer selected from the group consisting of:

alkali metal hydroxide, hydrochloric acid and alkaline earth metal hydroxide.

11. The method of claim 1, wherein the agitating step is performed with a blade-type impeller.

12. The method of claim 3, wherein the diffusing step is performed with an atomizer device driven by air impulses.

13. The method of claim 2, wherein the light crude oil has a specific gravity of 18.5 degrees API.

14. An emulsion suitable for transport through a pipeline comprising:

about 60% to about 85% by volume of a crude oil having a specific gravity from about 5 degrees to about 30 degrees API; and

about 40% to about 15% by volume of an aqueous solution comprising water and an emulsifier having a hydrophilic-lipophilic balance (HLB) value of about 13.5 to about 16, the emulsifier comprising anionic and non-ionic emulsifiers having a concentration from about 200 to about 10,000 parts per million by volume of the oil-in-water emulsion;

such that the viscosity is in the range from about 5 to 350 centipoise at a temperature of 100 degrees Fahrenheit; and

wherein the droplet size is substantially uniform and is no greater than about 20 micrometers when transport begins and no greater than about 70 micrometers up to 2000 hours later.

15. The emulsion of claim 14, wherein the non-ionic emulsifier has a concentration from about 500 to 5,000 parts per million.

16. The emulsion of claim 14, wherein the anionic emulsifier has a concentration from about 200 to 10,000 parts per million.

17. The emulsion of claim 14, wherein the emulsion further comprises a stabilizing agent.

18. The emulsion of claim 14, wherein the emulsion has a dynamic viscosity at ambient temperature of no more than about 50 Pa.s.

19. The emulsion of claim 14, wherein a particle size distribution in the emulsion has a sigma value of less than about 1.1.

20. A method of producing energy at a remote location comprising the steps of:

diffusing a hydrocarbon into an aqueous solution;

dispersing the hydrocarbon in the aqueous solution to produce an emulsion having a viscosity in the range from about 5 to 350 centipoise at a temperature of 100 degrees Fahrenheit and substantially uniform droplet sizes of no greater than about 40 micrometers, the emulsion comprising:

about 60% to about 85% by volume of the hydrocarbon having a specific gravity from about 5 degrees to about 30 degrees API; and

about 40% to about 15% by volume of the aqueous solution, the aqueous solution comprising water and an emulsifier having a hydrophilic-lipophilic balance (HLB) value of about 13.5 to about 16, the emulsifier comprising an anionic emulsifier and a non-ionic emulsifier and having a concentration from about 200 to about 10,000 parts per million by volume of the emulsion;

transporting the emulsion through a pipeline to the remote location; and

combusting the emulsion at the remote location.

21. A device for forming crude oil droplets of substantially uniform size in an emulsion comprising:

an inlet having at least one receiving passage connected to an end of a pipe;

a main body connected to the receiving passage for receiving crude oil from the pipe; and

a terminator connected to the main body having at least one exit passage;

such that oil droplets are elongated by the exit passages so as to form droplets of the substantially uniform size in the emulsion.

22. A device according to claim 21, wherein:

the main body further comprises a chamber having at least one sidewall passage, such that elongated droplets form by flowing into the chamber through the sidewall passages and out of the exit passage.

23. A device according to claim 21, wherein:

the main body has a cone shape; and

the terminator forms a disk at the large end of the cone shape.

* * * * *

United States Patent [19]
Hayes et al.

[11] Patent Number: 4,821,757
[45] Date of Patent: Apr. 18, 1989

[54] BIOEMULSIFIER STABILIZED
HYDROCARBOSOLS

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[21] Appl. No.: 65,124

[22] Filed: Jun. 23, 1987

Related U.S. Application Data

[60] Continuation of Ser. No. 780,779, Sep. 27, 1985, abandoned, which is a division of Ser. No. 653,808, Sep. 24, 1984, Pat. No. 4,684,372, which is a continuation-in-part of Ser. No. 547,892, Nov. 2, 1983, Pat. No. 4,618,348.

[51] Int. Cl.⁴ F17D 1/17

[52] U.S. Cl. 137/13; 252/8.551;
252/312

[58] Field of Search 252/8.551, 8.3; 137/13

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Attorney, Agent, or Firm—Pennie & Edmonds

[57] ABSTRACT

Methods and compositions are provided to facilitate the transportation and combustion of highly viscous hydrocarbons by forming reduced viscosity hydrocarbon-in-water emulsions, and in particular, bioemulsifier-stabilized hydrocarbon-in-water emulsions.

21 Claims, 9 Drawing Sheets

FIG. 1

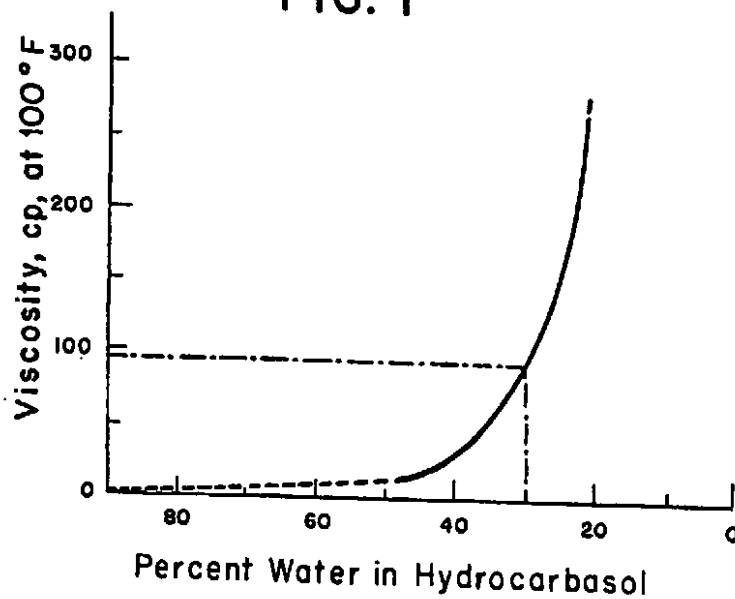


FIG. 8

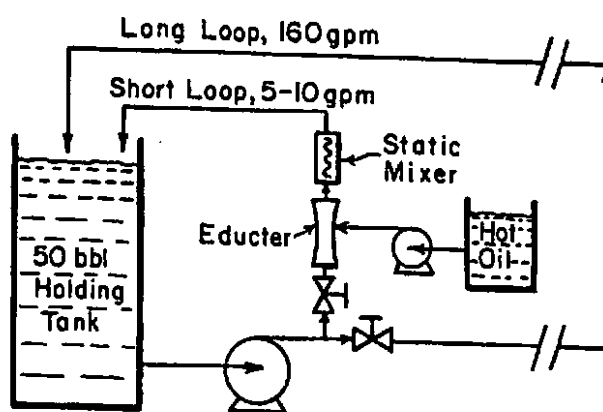
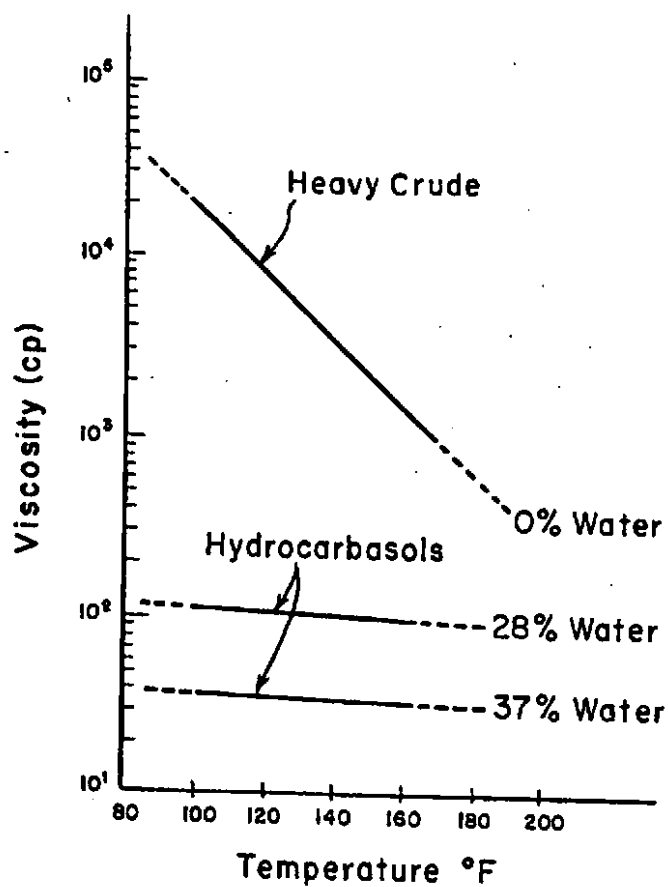


FIG. 2



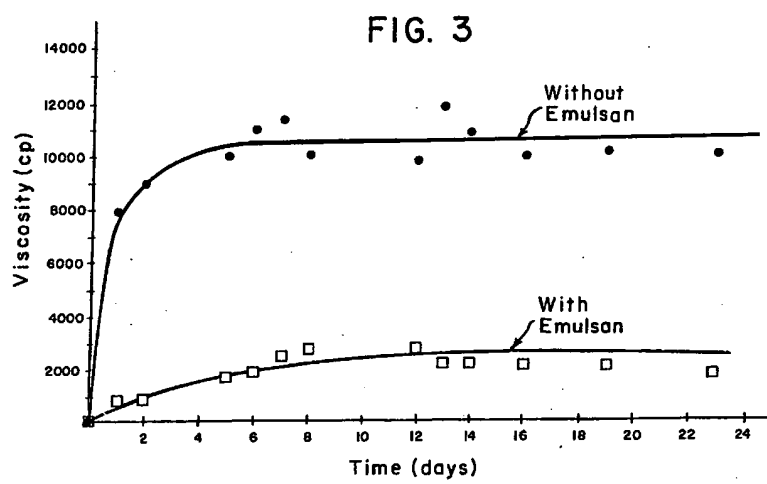
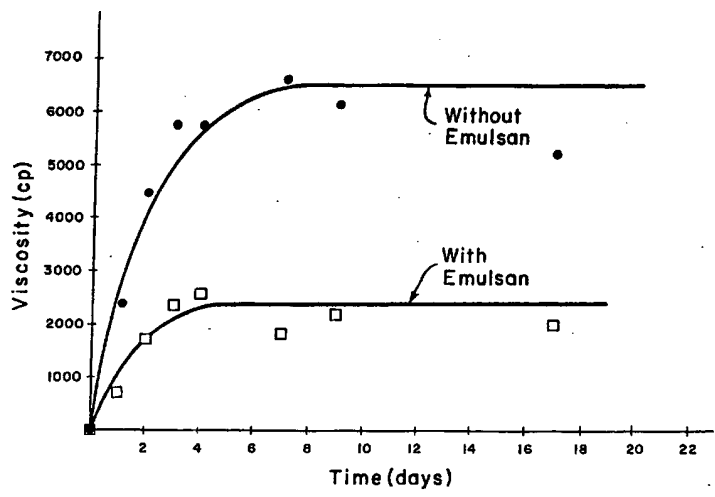
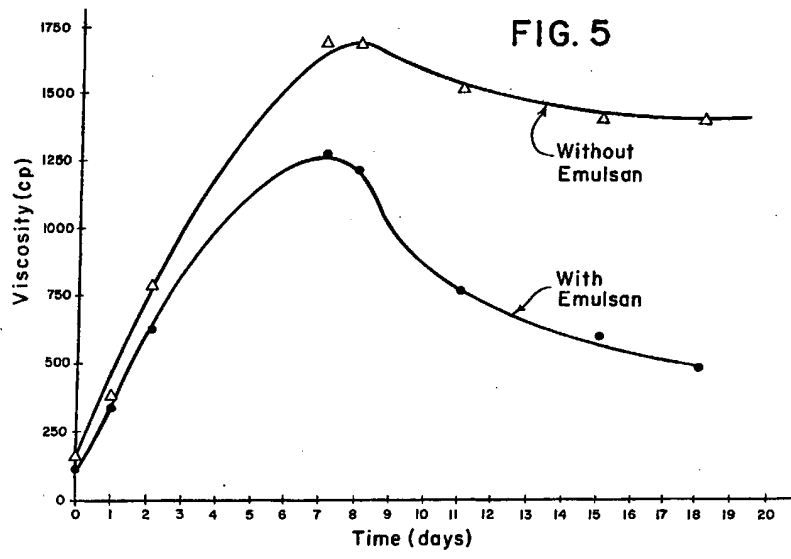


FIG. 4





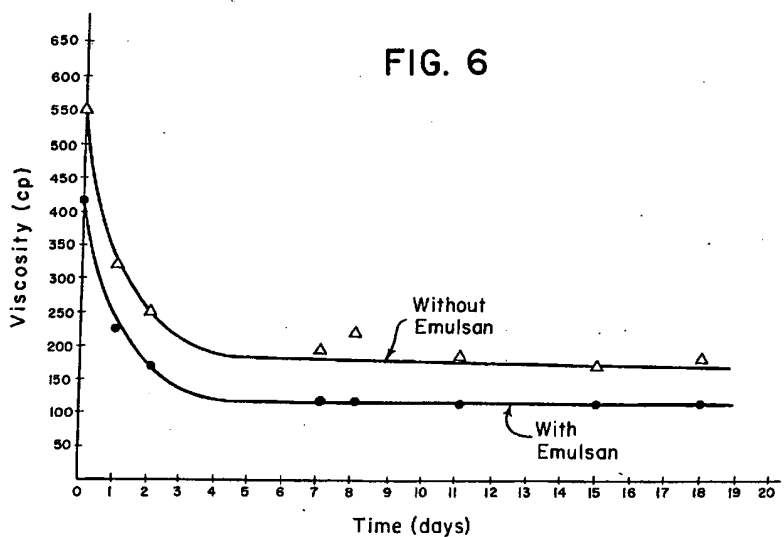


FIG. 7

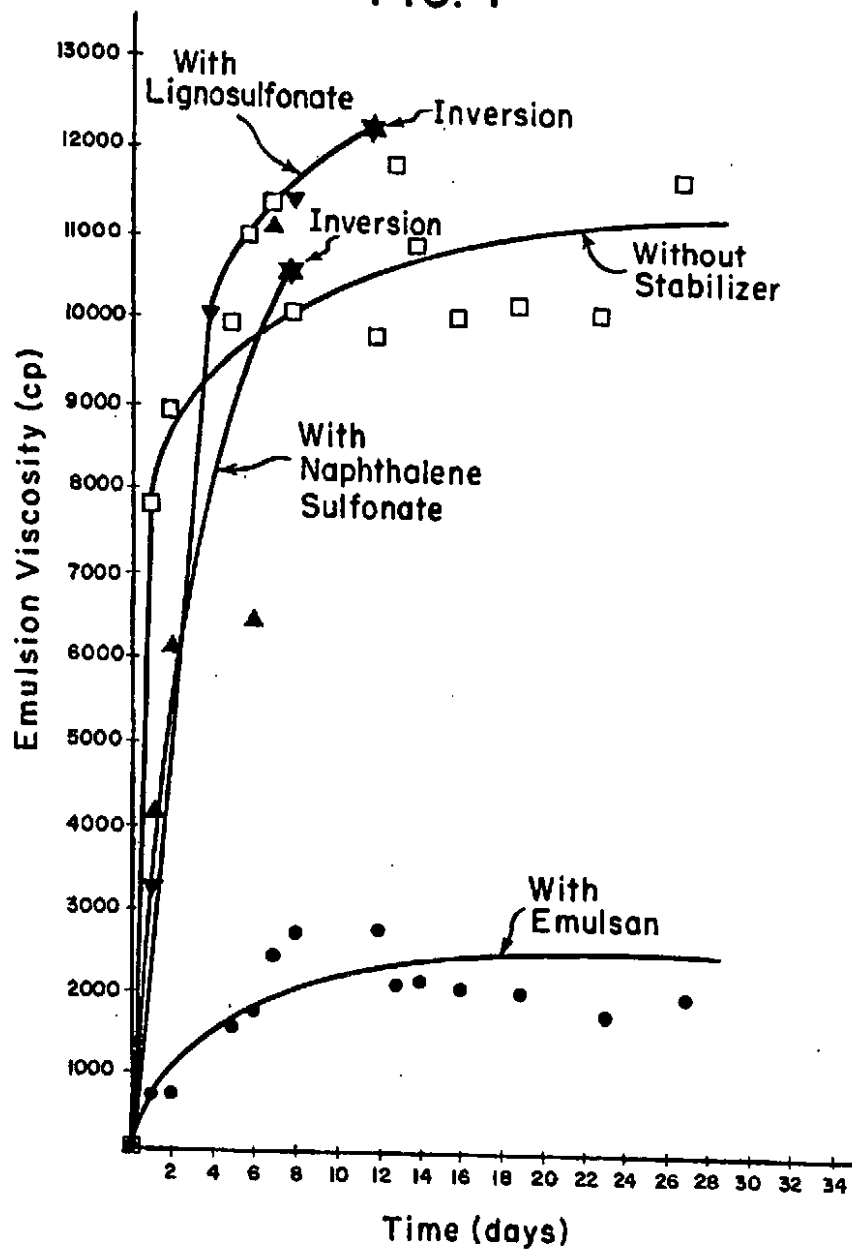


FIG. 9

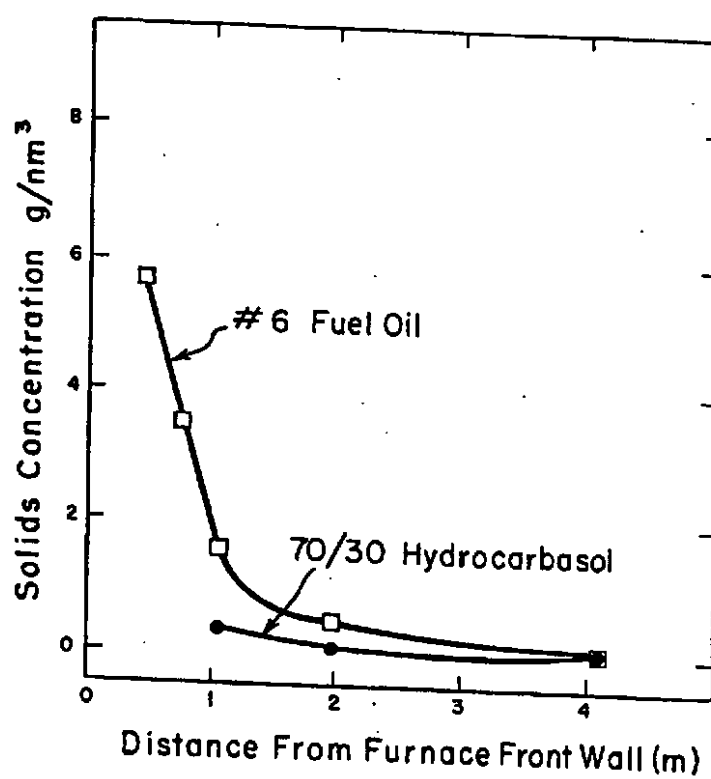
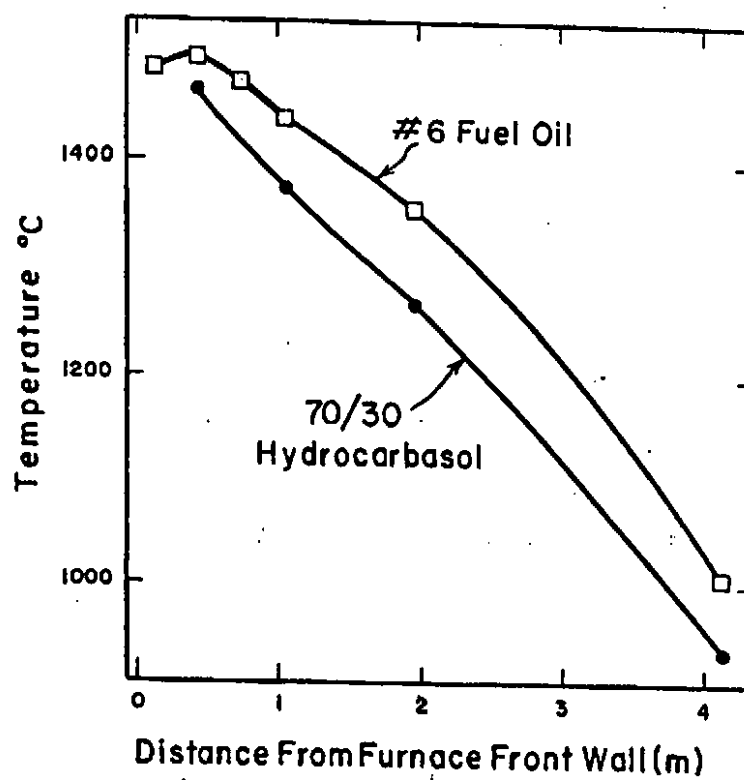


FIG. 10



BIOEMULSIFIER STABILIZED HYDROCARBOSOLS

This application is a continuation of application Ser. No. 780,779, filed Sept. 27, 1985, now abandoned, which is a division of application Ser. No. 653,808, filed Sept. 24, 1984, now U.S. Pat. No. 4,684,372 which in turn is a continuation-in-part of application Ser. No. 547,892, filed Nov. 2, 1983, now U.S. Pat. No. 4,618,348.

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1. INTRODUCTION

This invention relates to the utilization of highly viscous hydrocarbons, including heavy crude oils and residual oils. More particularly, this invention relates to the transportation of viscous hydrocarbons through the formation of low-viscosity bioemulsifier-stabilized hydrocarbon-in-water emulsions, or hydrocarbosols, in which the hydrocarbon droplets dispersed in the continuous aqueous phase are substantially stabilized from coalescence by the presence of bioemulsifiers and in particular, microbial bioemulsifiers, surrounding the droplets at the hydrocarbon/water interface. Furthermore, this invention relates to the combustion of pre-atomized fuels which include both hydrocarbosols and other viscous hydrocarbon-in-water emulsions.

Transportation of highly viscous hydrocarbons via conventional pipelines or other methods, including tankers and barges, presently cannot be accomplished practically without reduction of the viscosity of the hydrocarbons to put them into a pumpable form. This invention presents an alternative means to viscosity reduction, potentially more economical than methods requiring beating or dilution with lighter petroleum stocks. Formation of hydrocarbon-in-water emulsions effectively reduces the viscosity of heavy hydrocarbon materials, thereby facilitating shipping and pumping with conventional equipment, as well as in situ handling. Furthermore, the pre-atomized fuels formed by the methods of this invention can be burned directly by conventional means, without de-watering or demulsification, potentially resulting in emissions reductions.

Under circumstances where transportation distances from production location to utilization sites are considerable, giving rise to long transit times and/or the potential for shutdowns en route, or where long storage periods are required, the use of hydrocarbosols is especially advantageous. Because the microbial bioemulsifiers predominantly reside at the hydrocarbon/water interface, essentially covering the surface of the hydrocarbon droplets, the hydrocarbon droplets are effectively protected from coalescence and the reduced viscosity of the hydrocarbosols is effectively maintained over time. The substantial stability and improved pumpability of the hydrocarbosols allows them to be transported practically over long distances or remain stationary for long periods of time prior to utilization.

2. BACKGROUND OF THE INVENTION

2.1. Viscous Hydrocarbons

While large quantities of high-quality, relatively inexpensive, light crude oils presently are recoverable from world-wide geographical locations, ever-increasing consumption of petroleum fuels and other petroleum products and the energy crisis precipitated by such high demands have brought interest to bear on the enormous reserves of low-gravity, viscous hydrocarbons which also exist throughout the world. Viscous hydrocarbons present in natural deposits have been generally classified as viscous crude oils, bitumen or tar and have been variously called heavy crudes, native bitumen, natural bitumen, oil sands, tar sands, bituminous sands or deposits and natural asphalts, all of which materials are chemically gradational and nearly indistinguishable without standardized analysis. [For a discussion of the general characteristics of viscous hydrocarbons and the problem of precisely defining or classifying them, see Meyer, "Introduction" in: *The Future of Heavy Crude and Tar Sands*, p. 1, Mining Informational Services, McGraw Hill, Inc., New York (1981). See also Section 6.2 infra.]

The geographical distribution of heavy crude reserves is given in Table I [abstracted from Meyer and Dietzman (1981), "World Geography of Heavy Crude Oils," in: *The Future of Heavy Crude and Tar Sands*, pp. 16-28, Mining Informational Services, McGraw Hill, Inc., New York (1981)]. The total estimated figure for oil in place is 6200×10^9 barrels. Venezuela heads the list with roughly half of this total, 3000×10^9 barrels. Canada follows closely with 2950×10^9 barrels (this total includes hydrocarbon in bitumen), while the United States has an estimated 77×10^9 barrels. To put these figures in perspective, the total world reserves of oil lighter than 20°API is estimated to be about 660×10^9 barrels. Yet undiscovered reserves are estimated at 900×10^9 barrels. Thus, heavy crude is more plentiful than conventional oil by about a factor of four. Further considering the amount of heavy residual oils that result from the processing of conventional crudes, the amount of heavy oils that exists worldwide is very great indeed.

TABLE I
WORLD HEAVY OIL DEPOSITS
(Billions of Barrels)

Country	Resource	
	In-Place	Estimated Recoverable
Venezuela	3000	500
Canada	2950	213
United States	77	30
Italy	12	1
Madagascar	25	1
Iran	29	3
Iraq	10	1

It is clear that reserves of conventional light crudes are being depleted much faster than heavy crudes and that development of world reserves of viscous hydrocarbons will eventually become necessary to support world petroleum demands. Significant production of heavy crudes has begun, primarily by steam-assisted enhanced recovery methods. For example, recent estimates place production of heavy crude oil in California at 250,000 barrels per day. Future estimates [Barnea, "The Future of Heavy Crude and Tar Sands," in: *The Future of Heavy Crude and Tar Sands*, pp. 13-15, Mining Informational Services, McGraw Hill, Inc., New York (1981)] project that by the year 2000, production of heavy oil plus the bitumen from tar sands will increase to one-third of the world's total oil production. Such rapid development of heavy oil resources will extend the petroleum era and should: (1) allow products from heavy crudes to benefit from the existing energy infrastructure; (2) assure fuel supplies to the transportation sector and feed-stock to petrochemical plants; (3) be a stabilizing factor for world petroleum prices, increasing the number of oil producing countries; (4) reduce the strategic and political aspects of oil production; and (5) postpone the need for massive investments in coal conversion and other facilities for synthetic oil production.

2.2. Transportation of Viscous Hydrocarbons

The problem of transporting viscous hydrocarbons, be it out of a producing well, off a tanker or, especially, through a pipeline, is one of pumpability. Consequently, methods for transporting viscous hydrocarbons such as heavy crude oils have focused on modifying the oil into a pumpable form. Two general approaches have been considered. For waxy crudes, it is desirable to transport the oil above its pour point, i.e., above the temperature at which wax crystals in the oil inhibit its ability to flow. One method directed to this end is the use of pour-point depressants to reduce the pour point and maintain fluidity. Generally, this method is of value only with those oils of sufficiently low viscosities to permit transportation at ambient temperatures.

For highly viscous crudes, the approach taken has been to reduce the viscosity. When the crude is to be transported by pipeline, the viscosity must be sufficiently reduced to flow through conventional lines using conventional pumping equipment. Several methods have been used to reduce the viscosities of heavy crude oils for pipelining purposes. These methods include preparation of oil/solid slurries, mixing water with oil to form reduced viscosity emulsions, heating the oil to lower its viscosity and diluting the oil with low viscosity hydrocarbons such as condensate, gasoline, or naphtha [Sloan et al., "Pipeline Transportation of Heavy Oils," in: *The Future of Heavy Crude and Tar Sands*, pp. 719-726, Mining Informational Services, McGraw-Hill, Inc. New York (1981)].

Reported methods for reducing the viscosities of viscous hydrocarbons by forming oil-in-water emulsions for the purposes of transporting them through pipelines or pumping them from wells have involved the use of chemical additives. Among the chemicals which have been proposed or used are bases such as sodium hydroxide or ammonia [U.S. Pat. Nos. 3,380,531; 3,487,844; and 3,006,354], nonionic surfactants [U.S. Pat. Nos. 3,425,429 and 3,467,195] and combinations of nonionic and anionic surfactants [U.S. Pat. Nos. 4,239,052 and 4,249,554]. Instability of oil-in-water

emulsions can present a problem; for instance, oil-in-water emulsions are known to break or invert into unpumpable forms. Increasing the amount of chemicals used to maintain stability can result in prohibitive costs.

It is notable that in a recent review of methods for pipelining heavy crude oils (see Sloan et al.; supra) it was pointed out that there have been limited, if any, commercial applications of the emulsion approach to pipelining. It is also noteworthy that Sloan et al. concluded that the heating and dilution methods for reducing viscosity, despite the fact that they are energy-intensive and relatively costly, remain the major candidates for pipelining transport of heavy crude oils.

2.3. Combustion of Oil-In-Water Emulsions

The vast majority of combustible emulsions known in the art are water-in-oil emulsions, primarily consisting of relatively small amounts of water (1-10% by volume) in oil to enhance combustion. Some combustible oil-in-water emulsions have been described [see e.g., U.S. Pat. Nos. 3,958,915; 4,273,611 and 4,382,802]. Notably, however, the oil phases used have been light, low viscosity fuels and other low viscosity oils, e.g., kerosene, gasoline, gas oil, fuel oils and other oils which are liquid at room temperature. Combustible thixotropic jet fuels and other safety fuels have been described in U.S. Pat. Nos. 3,352,109; 3,490,237 and 4,084,940. Under resting (stationary) conditions, these oil-in-water emulsions are in the form of gels with apparent rest viscosities of 1000 cps and preferably 50,000-100,000 cps. These thixotropic oil-in-water emulsions exhibit low viscosities under high pumping (high shear) rates.

2.4. Microbial Surface Active Compounds

Many microbes can utilize hydrocarbon as their sole source of carbon for growth and energy production. The hydrocarbon substrates may be linear, branched, cyclic or aromatic. In order to rapidly assimilate such water-insoluble substrates, the microbes require a large contact area between themselves and the oil. This is achieved by emulsifying the oil in the surrounding aqueous medium. Hydrocarbon degrading microbes frequently synthesize and excrete surface active agents which promote such emulsification.

For example, the growth of *Mycobacterium rhodochrous* NCIB 9905 on n-decane yields a surface active agent which was reported by R.S. Holdom et al. [J. Appl. Bacteriol. 32, 448 (1969)] to be a nonionic detergent. J. Iguichi et al. [Agric. Biol. Chem., 33, 1657 (1969)] found that *Candida petrophilum* produced a surface active agent composed of peptides and fatty acid moieties, while T. Suzuki et al. [Agric. Biol. Chem., 33, 1919 (1969)] found trehalose lipid in the oil phase of culture broths of various strains of *Arthrobacter*, *Brevibacterium*, *Corynebacterium* and *Nocardia*. Wagner has reported the production of trehalose lipids by *Nocardia rhodochrous* and *Mycobacterium phlei* and their use in oil recovery [U.S. Pat. Nos. 4,392,892 and 4,286,660].

Torulopsis gropengiesseri was found to produce a sophorose lipid, while rhamnolipids are reported by K. Hisatsuka et al. [Agric. Biol. Chem., 35, 686 (1971)] to have been produced by *Pseudomonas aeruginosa* strain S7B1 and by S. Itoh et al. [Agric. Biol. Chem., 36, 2233

(1971)] to have been produced by another *P. aeruginosa* strain, KY4025. The growth of *Corynebacterium hydrocarbonclastus* on kerosene was reported by J.E. Zajic and his associates [Dev. Ind. Microbiol., 12, 87 (1971); Biotechnol. Bioeng., 14, 331 (1972); Chemosphere 1, 51 (1972); Crit. Rev. Microbiol., 5, 39; U.S. Pat. No. 3,997,398] to produce an extracellular heteropolysaccharide which, among other properties, emulsified kerosene, Bunker C fuel oil and other fuel oils.

Gutnick et al. discovered that *Acinetobacter calcoaceticus* ATCC 31012 (previously designated *Acinetobacter* sp. ATCC 31012 and also called RAG-1) produces interfacially active extracellular protein-associated lipopolysaccharide biopolymers called emulsans. These biopolymers are produced and build up as a capsule or outer layer around the bacterial cell during growth and are eventually released or sloughed off into the medium, from which they can be harvested as extracellular products. *Acinetobacter calcoaceticus* ATCC 31012 produces α -emulsans when grown on ethanol or fatty acid salts [U.S. Pat. Nos. 4,230,801; 4,234,689 and 4,395,354] and β -emulsans when grown on crude oil or hexadecane [U.S. Pat. No. 3,941,692]. The α -emulsans and β -emulsans can be derivatized to an O-deacylated form called psi-emulsans [U.S. Pat. No. 4,380,504]. The α -emulsans, β -emulsans and psi-emulsans can be deproteinized to yield apo- α -emulsans, apo- β -emulsans and apo-psi-emulsans, respectively [U.S. Pat. Nos. 4,311,830; 4,311,829 and 4,311,831, respectively].

Cooper and Zajic [Adv. Appl. Microbiol. 26:229-253 (1980)] have reviewed the production of surface active compounds by microorganisms. Some of the surface active agents described are listed in Table II.

TABLE II

MICROBIAL SURFACE ACTIVE COMPOUNDS

STRUCTURAL TYPE	PRODUCING MICROORGANISM(S)
<u>Carbohydrates-Lipids</u>	
Trehalose-Lipids	<i>Nocardia</i> , <i>Mycobacterium</i> , <i>Corynebacterium</i> , <i>Arthrobacter</i>
Rhamnolipids	<i>Pseudomonas aeruginosa</i>
Sophorose-Lipids	<i>Torulopsis</i> spp.
Polysaccharide-Lipid	<i>Candida tropicalis</i> , <i>Acinetobacter calcoaceticus</i>
<u>Amino Acid-Lipids</u>	
Lipopeptides	<i>Bacillus</i> , <i>Streptomyces</i> , <i>Corynebacterium</i> , <i>Mycobacterium</i>
Ornithine-Lipids	<i>Pseudomonas</i> , <i>Thiobacillus</i> , <i>Agrobacterium</i> , <i>Glucobacter</i>
Phospholipids	<i>Thiobacillus</i> , <i>Corynebacterium</i> , <i>Candida</i> , <i>Micrococcus</i>
Fatty Acids/Neutral Lipids	<i>Pseudomonas</i> , <i>Mycococcus</i> , <i>Penicillium</i> , <i>Aspergillus</i> , <i>Acinetobacter</i> , <i>Micrococcus</i> , <i>Candida</i>

3. SUMMARY OF THE INVENTION

This invention provides novel compositions and methods for manipulating viscous hydrocarbons including highly viscous crude and residual oils, generally characterized by API gravities of about 20° API or less, viscosities of about 100 centipoise or greater at 150° F., paraffin contents of about 50% by weight or less, and aromatic contents of about 15% or greater by weight.

into an emulsified form which (a) can be stored in facilities or transported by methods presently used to handle less viscous materials and (b) can be burned directly as quality combustible fuels. In an embodiment preferred for transportation purposes, the emulsified form of the viscous hydrocarbon is a hydrocarbosal defined as a bioemulsifier-stabilized hydrocarbon-in-water emulsion wherein the individual hydrocarbon droplets are essentially covered by water-soluble bioemulsifier molecules predominantly residing at the hydrocarbon/water interface, which bioemulsifier molecules form an effective barrier against droplet coalescence and hence promote the maintenance of discrete hydrocarbon droplets dispersed in a continuous, low-viscosity aqueous phase. The hydrocarbosals of this invention have viscosities reduced by at least a factor of about 10 and preferably at least 10^2 compared to that of the viscous hydrocarbon starting material, said hydrocarbosal viscosities remaining so reduced under static conditions for periods of at least about 1 day, and preferably at least about 30 days.

Surfactant packages for forming hydrocarbosals are provided which comprise a water-soluble chemical surfactant, or a combination of water-soluble chemical and/or biological co-surfactants, preferably nonionic and anionic surfactants, together with a bioemulsifier which, because of any number of characteristics including, but not limited to, high molecular weight, highly specific three-dimensional structure, hydrophobic and hydrophilic nature, polymeric nature and/or sparing solubility in hydrocarbons, binds tightly to the hydrocarbon/water interface and essentially covers the surface of individual hydrocarbon droplets in hydrocarbon-in-water emulsions, effectively maintaining discrete droplets and preventing coalescence and imparting substantial stability to hydrocarbon-in-water emulsions.

Methods are provided for transporting viscous hydrocarbons wherein a surfactant package is used in a proportion from about 1:100 to about 1:20,000 based on oil to form a hydrocarbosal containing up to about 90% by volume of hydrocarbon in an aqueous phase variously comprising deionized water, municipal water, brines or alcohol/water mixtures, which hydrocarbosal can be shipped by conventional means or pumped through conventional, non-heated pipelines.

Methods are also provided for utilizing viscous hydrocarbons by forming pre-atomized fuels, i.e., hydrocarbosal fuels or hydrocarbon-in-water emulsion fuels and burning them in conventional combustion facilities.

4. NOMENCLATURE

The term "hydrocarbosal" is defined as any bioemulsifier-stabilized hydrocarbon-in-water emulsion wherein the individual hydrocarbon droplets are essentially surrounded or covered by water-soluble bioemulsifier molecules predominantly residing at the hydrocarbon/water interface, which bioemulsifier molecules form an effective barrier against droplet coalescence and hence promote the maintenance of discrete hydrocarbon droplets suspended or dispersed in the continuous, low-viscosity aqueous phase.

The term "water-soluble" is defined to include water-dispersible substances.

The term "viscous hydrocarbon" is defined as any naturally occurring crude oil or any residual oil remaining after refining operations which is generally characterized by a viscosity of about 10^2 – 10^6 centipoise or greater and otherwise generally, but not necessarily, characterized by an API gravity of about 20° API or less, high metal content, high sulfur content, high asphaltene content and/or high pour point. The term "viscous hydrocarbon," it is to be understood, also encompasses the following nomenclature: vacuum residuals, vis-breaker residuals, catalytic-cracker residuals, catalytic hydrogenated residuals, coker residuals, ROSE (residual oil supercritical extraction) residuals, tars and cut-back tars, bitumen, pitch and any other terms describing residuals of hydrocarbon processing.

The term "pre-atomized fuel" is defined as any hydrocarbosal and any viscous hydrocarbon-in-water emulsion formed by methods described herein for use as a combustible fuel.

The term "bioemulsifier" is defined as any biologically derived substance which, by virtue of any combination of characteristics including, but not limited to, high molecular weight, polymeric nature, highly specific three-dimensional structure, hydrophobic and hydrophilic moieties and sparing solubility in hydrocarbons, binds tightly to the hydrocarbon/water interface and essentially covers the surface of individual hydrocarbon droplets in hydrocarbon-in-water emulsions, effectively maintaining discrete droplets and preventing coalescence, and thereby imparting substantial stability to hydrocarbon-in-water emulsions. An example of a bioemulsifier is α -emulsan.

The term "biosurfactant" is defined as any biologically derived substance which reduces the interfacial tension between water and a hydrocarbon and, as a result, reduces the energy requirement (mixing energy) for creation of additional interfacial area. An example of a biosurfactant is a glycolipid.

The term "surfactant package" is defined as any composition useful for forming hydrocarbon-in-water emulsions of viscous hydrocarbons generally characterized by a paraffin content of about 50% by weight or less and an aromatic content of about 15% by weight or greater with viscosities of about 100 centipoise or greater at 150° F., which composition may comprise a chemical surfactant or a combination of chemical co-surfactants or a combination of co-surfactant(s) and biosurfactant(s) or a combination of chemical surfactant(s) and bioemulsifier(s) or a combination of chemical surfactant(s), biosurfactant(s) and bioemulsifier(s), and which may also include chemical emulsion stabilizers, and which may be in aqueous form.

The term "emulsans," which reflects the polysaccharide structure of these compounds and the exceptional bioemulsifier activity of these materials, generically identifies those capsular/extracellular microbial protein-associated lipoheteropolysaccharides produced by *Acinetobacter calcoaceticus* ATCC 31012 and its derivatives or mutants, which may be subdivided into the

α -emulsans and the β -emulsans. The name "apoemulsan" generically identifies those deproteinized lipopolysaccharides obtained from the emulsans.

The term " α -emulsans" defines those extracellular microbial protein-associated lipopolysaccharides produced by *Acinetobacter calcoaceticus* ATCC 31012 and its derivatives or mutants in which the lipopolysaccharide components (i.e., without the associated protein) are completely N-acylated and partially O-acylated heteropolysaccharides made up of major amounts of D-galactosamine and an aminouronic acid, the lipopolysaccharide components containing at least 5 percent by weight of fatty acid esters in which (1) the fatty acids contain from about 10 to about 18 carbon atoms; and (2) about 50 percent by weight or more of such fatty acids are composed of 2-hydroxydodecanoic acid and 3-hydroxydodecanoic acid. It follows, therefore, that the deproteinized β -emulsan are called "apo- β -emulsans."

The term "psi-emulsans" defines those extracellular microbial protein-associated lipopolysaccharides produced by *Acinetobacter calcoaceticus* ATCC 31012 and its mutants in which the lipopolysaccharide components (i.e., without the associated protein) are completely N-acylated and partially O-acylated heteropolysaccharides made up of major amounts of D-galactosamine and an aminouronic acid, the lipopolysaccharide components containing less than 5 percent by weight of fatty acid esters in which (1) the fatty acids contain from about 10 to about 18 carbon atoms; and (2) less than 50 percent by weight of such fatty acids are composed of 2-hydroxydodecanoic acid. The deproteinized β -emulsans are called "apo- β -emulsans."

The term "psi-emulsans" defines the O-deacylated extracellular protein-associated microbial polysaccharides obtained from the emulsans, the protein-free components of such psi-emulsans being completely N-acylated heteropolysaccharides made up of major amounts of D-galactosamine and an aminouronic acid and containing from 0 to 1 percent of fatty acid esters in which, when present, the fatty acids contain from about 10 to about 18 carbon atoms. These protein-free components are called "apo-psi-emulsans," regardless of how they are prepared.

The term "polyanionic heteropolysaccharide biopolymers" defines those biopolymers in which (a) substantially all of the sugar moieties are N-acylated aminosugars, a portion of which is N-acylated-D-galactosamine and another portion of which is N-acylated aminouronic acid, a part of the N-acyl groups of such heteropolysaccharide being N-3-hydroxydodecanoyl groups; and (b) at least 0.2 micromoles per milligram of such heteropolysaccharide consist of fatty acid esters in which (1) the fatty acids contain about 10 to about 18 carbon atoms and (2) about 50 percent by weight or higher of such fatty acids are composed of 2-hydroxydodecanoic acid and 3-hydroxydodecanoic acid.

5. BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a graphical representation of the viscosity versus water content profile of emulsan-stabilized hydrocarbons formulated with Boscan crude oil,

wherein the dashed line (at 30% water) indicates near-optimum operating conditions;

FIG. 2 is a graphical representation of the viscosity versus temperature profiles for a heavy crude oil (Boscan) and two emulsan-stabilized hydrocarbons formulated with Boscan crude oil;

FIG. 3 is a graphical representation of the viscosity versus time profiles for two emulsions formulated with a Texas fireflood crude oil and a surfactant package comprising a nonionic surfactant and an anionic surfactant, showing the effect on viscosity of the addition of emulsan to the surfactant package;

FIG. 4 is a graphical representation of the viscosity versus time profiles for two emulsions formulated with a Texas fireflood crude oil and a surfactant package comprising a nonionic surfactant, showing the effect on viscosity of the addition of emulsan to the surfactant package;

FIG. 5 is a graphical representation of the viscosity versus time profiles for two emulsions formulated with a Kansas crude oil and tap water using a surfactant package comprising a nonionic surfactant and an anionic surfactant, showing the effect on viscosity of the addition of emulsan to the surfactant package;

FIG. 6 is a graphical representation of the viscosity versus time profiles for two emulsions formulated with a Kansas crude oil and Texas brine using a surfactant package comprising a nonionic surfactant and an anionic surfactant, showing the effect on viscosity of the addition of emulsan to the surfactant package;

FIG. 7 is a graphical representation of the viscosity versus time profiles for four emulsions formulated with a Texas fireflood crude oil and a surfactant package comprising a nonionic surfactant and an anionic surfactant, comparing the effect on viscosity of the addition of an emulsion stabilizer (emulsan, or the commonly used emulsion stabilizers, lignin sulfonate and naphthalene sulfonate) to the surfactant package;

FIG. 8 is a schematic representation of a pilot system used for forming and pumping a hydrocarbonol through a three-inch pipeline;

FIG. 9 is a graphical representation of the changes in solids concentration along the frame axis during combustion of a Number 6 fuel oil and a pre-atomized fuel made from Number 6 fuel oil as a function of distance from the front wall of the furnace; and

FIG. 10 is a graphical representation of the variation of axial flame temperatures during combustion of a Number 6 fuel oil and a pre-atomized fuel made from Number 6 fuel oil as a function of distance from the front wall of the furnace.

6. DETAILED DESCRIPTION OF THE INVENTION

6.1. Surfactant Packages

The surfactant packages of this invention can be formulated with a wide variety of chemical and microbial surface active agents and are preferably formulated with water-soluble surface active agents to provide for the formation of oil-in-water, as opposed to water-in-oil, emulsions. The surfactant packages can be formulated

with numerous chemical surfactants, used alone or in conjunction with chemical co-surfactants of the same type (e.g., a combination of water-soluble nonionic surfactants) or of different types (e.g., a combination of water-soluble nonionic, anionic, cationic and/or amphoteric surfactants), and can be further formulated in combination with (a) a water-soluble biosurfactant or combination of biosurfactants as co-surfactant(s) and/or (b) a water-soluble bioemulsifier or combination of bioemulsifiers as emulsion stabilizer(s). In certain instances, chemical emulsion stabilizers may also be used in place of bioemulsifiers. It is also possible to formulate surfactant packages comprising only microbial surface active agents, i.e., combinations of biosurfactants and bioemulsifiers. The surfactant packages of this invention vary with the type of viscous oil to be emulsified. The following general compositions are offered by way of illustration. For viscous crudes, surfactant packages can be formulated to comprise at least one chemical surfactant and at least one bioemulsifier. They can also be formulated to comprise at least one water-soluble non-ionic surfactant, at least one water-soluble anionic surfactant, and at least one bioemulsifier. For viscous residuals, surfactant packages can be formulated to comprise at least one water-soluble non-ionic surfactant or at least one anionic surfactant or combinations of non-ionic surfactants and anionic surfactants and which can further comprise biosurfactants and/or bioemulsifiers.

The types of water-soluble nonionic chemical surfactants suitable for use in the surfactant packages are listed in Table III.

TABLE III

CLASSES AND SUBCLASSES OF
NONIONIC CHEMICAL SURFACTANTS

Alcohols, ethoxylated
Alkylphenols, ethoxylated
Carboxylic Esters, ethoxylated
Glycerol Esters
Polyethylene Glycol Esters
Anhydrosorbitol Esters
Ethoxylated Anhydrosorbitol and Sorbitol Esters
Natural Fats and Oils, ethoxylated
Ethylene and Diethylene Glycol Esters
Propanediol Esters
Other Carboxylic Acid Esters
Carboxylic Amides, Ethoxylated
Amines, polyoxyalkylated

In surfactant packages for viscous crudes, the preferred water-soluble nonionic chemical surfactants are ethoxylated alkyl phenols and ethoxylated alcohols. In surfactant packages for viscous residuals, the preferred water-soluble nonionic surfactants are, again, ethoxylated alkyl phenols and also polyoxyalkylated amines. The ethoxylated alkyl phenols are of the general formula:



wherein R represents an alkyl group containing from about 8 to about 12 carbon atoms (i.e., about C₈ to about C₁₂), x represents the number of alkyl groups and is either 1 or 2, and wherein n represents the number of ethoxy groups (moles ethylene oxide) which can range from about 1 to about 100. [For a list of commercially

available ethoxylated alkylphenols, see "Surfactants and Detergent Systems" in: Encyclopedia of Chemical Technology, Kirk-Othmer (Third Edition), Volume 22, pp. 366-367, John Wiley & Sons, New York (1983).] In surfactant packages for viscous crudes, preferred ethoxylated alkyl phenols are those having R groups of 8 or 9 carbon atoms and having from about 7 to about 100 ethoxy groups. An example of a particularly preferred ethoxylated alkyl phenol is monononylphenol with about 40 ethoxy groups. In surfactant packages for viscous residuals, preferred ethoxylated alkyl phenols are those having alkyl groups of 8 or 9 carbon atoms and having from about 9 to about 70 ethoxy groups. An example of a particularly preferred ethoxylated alkyl phenol for use with viscous residuals in monooctylphenol with about 16 ethoxy groups.

The ethoxylated alcohols are of the general formula:



wherein R represents an aliphatic group (linear or branched) containing from about 6 to about 18 carbon atoms and wherein n represents the number of ethoxy groups which can range from about 2 to about 100. [For a list of commercially available ethoxylated alcohols, see "Surfactants and Detergent Systems" in: Encyclopedia of Chemical Technology, supra, pp. 364-365.] Examples of ethoxylated alcohols include ethoxylated trimethylnonanol with about 3 to about 9 ethoxy groups and ethoxylated secondary alcohols having R groups of about 11 to about 15 carbon atoms with about 3 to about 30 ethoxy groups, but preferably greater than about 7 ethoxy groups.

The polyoxyalkylated amines are of the general formula:



wherein R represents an oxyalkyl group containing either 2 or 3 carbon atoms. These R groups can range in number from about 4 to about 500, and that number is represented by x. The number of nitrogen atoms is represented by y and preferably ranges from about 1 to about 2; the alkyl group is preferably ethyl (C₂H₅). Preferred polyoxyalkylated amines are those having R groups of 2 or 3 carbon atoms and having from about 50 to about 450 oxyalkyl groups. An example of a particularly preferred polyoxyalkylated amine is a polyoxyalkylated diamine with about 50 ethoxy groups and about 60 propoxy groups.

The types of water-soluble anionic chemical surfactants suitable for use in the surfactant packages of this invention are listed in Table IV.

TABLE IV

CLASSES AND SUBCLASSES OF
ANIONIC CHEMICAL SURFACTANTS

Carboxylic Acids and Salts
Sulfonic Acids and Salts
Lignosulfonates
Alkylbenzenesulfonates
Alkylbenzenesulfonates, polymerized
Alkylarylsulfonates, short chain
Alkylarylsulfonates, polymerized

TABLE IV-continued
CLASSES AND SUBCLASSES OF
ANIONIC CHEMICAL SURFACTANTS

Naphthalenesulfonates
Alkyl naphthalenesulfonates, polymerized
Naphthalene/formaldehyde condensate polymers
Petroleum Sulfonates
Sulfonates with ester, ether, or amide linkages
(dialkyl sulfosuccinates)
Other Sulfonates
Sulfuric Acid Esters and Salts
Alcohols, sulfated
Alcohols, ethoxylated and sulfated
Alkylphenols, ethoxylated and/or sulfated
Acids, Amides, and Esters, sulfated
Natural Fats and Oils, sulfated
Phosphoric and Polyphosphoric Acid Esters (and Salts)
Alcohols and Phenols, alkoxylated and
phosphated (and their salts)
Other Phosphoric and Polyphosphoric Acid
Esters (and their salts)
Carboxylic Acid Esters

In surfactant packages for both viscous crudes and viscous residuals, the preferred water-soluble anionic chemical surfactants are sulfonated or sulfated forms of nonionic surfactants. In surfactant packages for viscous crudes, ethoxylated alcohol sulfates are preferred. In surfactant packages for viscous residuals, sulfonated or sulfated ethoxylated alkylphenols and ethoxylated alcohol sulfates are preferred. In surfactant packages for both viscous crudes and viscous residuals, alkylaryl sulfonates are also preferred anionic chemical surfactants. The ethoxylated and sulfated alcohols are of the general formula:



wherein R represents an aliphatic group containing from about 6 to about 16 carbon atoms, preferably from about 12 to about 14, n represents the number of ethoxy groups which can range from about 1 to about 4, preferably from about 2 to about 3, and M includes, but is not limited to, ammonium (NH₄), sodium (Na), potassium (K), calcium (Ca) or triethanolamine, preferably ammonium. [For a list of commercially available ethoxylated alcohol sulfates, see "Surfactants and Detergent Systems" in: Encyclopedia of Chemical Technology, supra, p. 357.] The alcohol moiety of the ethoxylated alcohol sulfate can be an even or odd number or mixture thereof. In surfactant packages for viscous crudes, an example of a particularly preferred ethoxylated alcohol sulfate is poly(3)ethoxy C₁₂-C₁₄ linear primary alcohol sulfate, ammonium salt. It is also possible to use nonethoxylated alcohol sulfates, i.e., alcohol sulfates of the formula R(OC₂H₅)_nOSO₃M as described supra but wherein n=0. In surfactant packages for viscous residuals, an example of a particularly preferred nonethoxylated alcohol sulfate is the sodium salt of a sulfated lauryl alcohol.

The sulfated ethoxylated alkylphenols are of the general formula:



wherein R represents an aliphatic group containing at least about 8 or 9 carbon atoms, n represents the number

of ethoxy groups which can range from about 1 to about 100, preferably from about 4 to about 9 and M includes, but is not limited to, ammonium (NH₄), sodium (Na), potassium (K) and calcium (Ca) or triethanolamine (TEA), preferably ammonium.

An example of a particularly preferred sulfated ethoxylated alkylphenol is the ammonium salt of a sulfated nonylphenol ethoxylate containing, but not limited to, about 4 ethoxy groups.

The alkylaryl sulfonates are of the general formula:



wherein Ar is an aromatic group which is benzyl, naphthyl, phenyl, tolyl, xylyl or ethylphenyl, R is a linear or branched chain alkyl group containing from about 2 to about 16 carbon atoms, n is 1 or 2, m is 1 or greater, x is at least about 1, and M includes, but is not limited to, ammonium, sodium, potassium, calcium or triethanolamine. [For a list of commercially available alkylaryl sulfonates, see "Surfactants and Detergent Systems" in: Encyclopedia of Chemical Technology, supra, p. 358.] An example of an alkylaryl sulfonate is a modified amine dodecylbenzene sulfonate. In surfactant packages for viscous residuals, an example of a particularly preferred alkylaryl sulfonate is the sodium salt of polymerized alkyl naphthalene sulfonate.

The preferred water-soluble microbial surface active agents for use in the surfactant packages of this invention are any microbial or other biologically-derived substances which function as bioemulsifiers, i.e., substances which, by virtue of such characteristics as large molecular weight, polymeric nature, highly specific three-dimensional structure, hydrophobic and hydrophilic nature, and sparing solubility in oil, effectively cover the oil/water interface maintaining discrete, individual oil droplets in oil-in-water emulsions thereby substantially stabilizing emulsions from coalescence. Among the preferred bioemulsifiers are heteropolysaccharide biopolymers produced by bacteria of the genus *Acinetobacter* and the genus *Arthrobacter*, and in particular, those produced by strains of *Acinetobacter calcoaceticus*. Such *Acinetobacter* heteropolysaccharide biopolymers include, but are not limited to, polyanionic heteropolysaccharide biopolymers, α-emulsans, β-emulsans, psi-emulsans, apo-α-emulsans, apo-β-emulsans and apo-psi-emulsans produced by *Acinetobacter calcoaceticus* ATCC 31012 (deposited at the American Type Culture Collection in Rockville, MD) defined in Section 4 and described in U.S. Pat. Nos. 4,395,353; 4,395,354; 3,941,692; 4,380,504; 4,311,830; 4,311,829; and 4,311,831, respectively (hereby incorporated by reference). Other *Acinetobacter calcoaceticus* materials that can be used are the products of strains NS-1 (NRRL B-15847), NS-4 (NRRL B-15848), NS-5 (NRRL B-15849), NS-6 (NRRL B-15860) and NS-7 (NRRL B-15850). The foregoing "NS" strains have been deposited at the Northern Regional Research Center in Peoria, IL and have been assigned the foregoing NRRL accession numbers. The "NS" strains of *Acinetobacter calcoaceticus* are described by Sar and Rosenberg,

Current Microbiol. 9(6):309-314 (1983), hereby incorporated by reference. Other *Acinetobacter* heteropolysaccharide biopolymers are those produced by *Acinetobacter calcoaceticus* BD4 [Taylor and Juni, J. Bacteriol. 81: 688-693 (1961), hereby incorporated by reference]. Particularly preferred *Acinetobacter* heteropolysaccharide biopolymers are the α -emulsans, the production of which is further described in U.S. Pat. Nos. 4,230,801 and 4,234,689 (hereby incorporated by reference). The α -emulsans are characterized by a Specific Emulsification Activity of about 200 units per milligram or higher, where one unit per milligram of Specific Emulsification Activity is defined as that amount of emulsifying activity per milligram of bioemulsifier which yields 100 Klett absorption units using a standard hydrocarbon mixture consisting of 0.1 ml of 1:1 (v/v) hexadecane/2-methylnaphthalene and 7.5 ml of Tris-Magnesium buffer.

The foregoing *Acinetobacter* bioemulsifiers can be used in the surfactant packages of this invention in a variety of forms including, but not limited to, post-fermentation whole broth; cell-free (Millipore-filtered, e.g.) or partially cell-free supernatants of post-fermentation culture broth; the cells themselves; protease-treated, liquid or dried materials; and protease-treated, ultrafiltered, liquid or dried materials.

Numerous other microbial organisms may possibly serve as a source of biological surface active agents, including biosurfactants and bioemulsifiers, for use in the surfactant packages of this invention. Some of these microorganisms and the types of compounds they produce are listed in Table V, though the list is not exhaustive. The surfactant packages of this invention may also be formulated with water-soluble cationic chemical surfactants, including, but not limited to, oxygen-free amines, oxygen-containing amines, amide-linked amines and quaternary ammonium salts. Use of cationic chemical surfactants in conjunction with microbial surface active agents would require that the charge characteristic of the biological compounds be considered. For example, cationic chemical surfactants would probably best be used in conjunction with neutral microbial surface active agents and would probably best not be used in conjunction with the preferred polyanionic heteropolysaccharide bioemulsifiers.

TABLE V

MICROBIAL SURFACE ACTIVE AGENTS

Microbial Compound	Microbial Source
Carbohydrate-containing surface active agents	
Trehalose lipids	<i>Arthrobacter</i> spp. <i>Arthrobacter paraffinus</i> KY4303 <i>Mycobacterium</i> spp. <i>Mycobacterium smegmatis</i> <i>Mycobacterium kansasii</i> <i>Mycobacterium tuberculosis</i> <i>Mycobacterium phlei</i> <i>Mycobacterium rhodochrous</i> <i>Mycobacterium fortuitum</i> <i>Nocardia</i> spp. <i>Nocardia asteroides</i> <i>Nocardia rhodochrous</i> <i>Corynebacterium</i> spp. <i>Corynebacterium diphtheriae</i> <i>Brevibacterium</i>
Rhamnolipids	<i>Arthrobacter paraffinus</i> <i>Pseudomonas aeruginosa</i>

TABLE V-continued

MICROBIAL SURFACE ACTIVE AGENTS

Microbial Compound	Microbial Source
5 Sophorose lipids	<i>Torulopsis</i> spp. <i>Torulopsis magnoliae</i> <i>Torulopsis greggii</i> <i>Lactobacillus fermenti</i>
Diglycosyl diglycerides	
Polysaccharide-lipid complexes	<i>Arthrobacter</i> spp. <i>Candida tropicalis</i>
10 Amino acid-containing surface active agents	
Lipopeptides	<i>Bacillus subtilis</i> <i>Bacillus mesentericus</i> <i>Candida petrophilum</i> <i>Streptomyces canis</i> <i>Corynebacterium lepus</i> <i>Nocardia asteroides</i> <i>Mycobacterium paratuberculosis</i> <i>Mycobacterium fortuitum</i> <i>Pseudomonas rubescens</i> <i>Thiobacillus thiooxidans</i> <i>Agrobacterium tumefaciens</i> <i>Gluconobacter cerinus</i> <i>Pseudomonas aeruginosa</i> <i>Thiobacillus thiooxidans</i> <i>Corynebacterium lepus</i> <i>Corynebacterium alkalescens</i> <i>Candida tropicalis</i> <i>Micrococcus cerificans</i>
Ornithine lipids	
20 Protein	
Phospholipids	
25 Fatty acids and Neutral lipids	
Carboxylic acids	<i>Corynebacterium lepus</i> <i>Pseudomonas</i> spp. <i>Mycococcus</i> spp. <i>Penicillium</i> spp. <i>Aspergillus</i> spp. <i>Acinetobacter</i> spp. <i>Micrococcus cerificans</i> <i>Candida cloacae</i> <i>Mycobacterium rhodochrous</i> <i>Arthrobacter paraffinus</i> <i>Arthrobacter paraffinus</i> ATCC 19358 <i>Mycobacterium lacticum</i> <i>Acinetobacter</i> spp. <i>Thiobacillus thiooxidans</i>
35 Neutral lipids and mixtures of fatty acids	
40 Polysaccharides	
Heteropolysaccharides	<i>Xanthomonas campestris</i> <i>Xanthomonas campestris</i> NRRL B1459 <i>Arthrobacter viscosus</i> <i>Arthrobacter viscosus</i> NRRL B1973 <i>Methylobacterium</i> spp. <i>Lactobacillus</i> spp. <i>Methylobacterium massii</i> NRRL B5696 <i>Acinetobacter calcoaceticus</i> <i>Acinetobacter calcoaceticus</i> ATCC 31012 <i>Pseudomonas fluorescens</i> <i>Yersinia pseudotuberculosis</i> <i>Yersinia pestis</i> <i>S. calcoaceticus</i>
45 Homopolysaccharides	
50 Lipopolysaccharides	
55 Other Surface Active Agents	unknown or poorly characterized
60	<i>Pseudomonas</i> spp. <i>Pseudomonas aeruginosa</i> <i>Pseudomonas oleovorans</i> <i>Pseudomonas putida</i> <i>Pseudomonas desmolyticum</i> <i>Pseudomonas methanica</i> <i>Corynebacterium</i> spp. <i>Corynebacterium</i> sp. ATCC 21235 <i>Corynebacterium hydrocarbonoclasticus</i> UW0409 <i>Bacillus subtilis</i> <i>Bacillus hexacarborum</i> <i>Candida</i> spp. <i>Candida utilis</i> <i>Candida utilis</i> ATCC 9216
65	

TABLE V-continued

MICROBIAL SURFACE ACTIVE AGENTS	
Microbial Compound	Microbial Source
	<i>Candida guilliermondii</i>
	<i>Candida rugosa</i>
	<i>Candida lipolytica</i>
	<i>Aspergillus niger</i>
	<i>Aspergillus versicolor</i>
	<i>Desulfotribrio hydrocarbono-</i>
	<i>chloricus</i>
	<i>Desulfotribrio desulfuricans</i>
	<i>Endomycopsis lipolytica</i>
	<i>Saccharomycopsis lipolytica</i>
	<i>Aerobacter aerogenes</i>
	<i>Aerobacter acid</i>
	<i>Aerobacter peracydans</i>
	<i>Alcaligenes entrophus</i>
	<i>Achromobacter</i> spp.
	<i>Achromobacter</i> sp. ATCC 21910
	<i>Achromobacter agilis</i>
	<i>Achromobacter tropacetratum</i>
	<i>Actinomyces oligosaccharophilus</i>
	<i>Aureobasidium pullulans</i>
	<i>Arthrobacter</i> sp. ATCC 21908
	<i>Micrococcus</i> spp.
	<i>Micrococcus</i> sp. ATCC 21909
	<i>Micrococcus cerefaens</i> ATCC 14987

Surfactant packages can be formulated from nonionic chemical surfactants or combinations of nonionic and anionic chemical surfactants (preferably in about a 1:1 ratio by weight) without bioemulsifiers but preferably, for emulsion stabilization, with bioemulsifiers in the range of about 1% to about 50% by weight. Surfactant packages comprising bioemulsifiers in the range of about 10% to about 20% by weight and particularly around 15% by weight are preferred. Examples of surfactant packages are: (a) about 10% to about 15% α -emulsan by weight in combination with ethoxylated secondary alcohols having carbon chains of about 11 to about 15 carbon atoms in length [e.g., Tergitol 15-S-X (Union Carbide Corp.)], where X represents the number of moles of ethylene oxide and is preferably greater than 7; (b) about 10% to about 15% α -emulsan by weight in combination with about 20% to about 25% by weight of an ethoxylated trimethylinonanol [e.g., Tergitol TMN-6 (Union Carbide Corp.)] and about 60% to about 70% by weight of an ethoxylated alkyl phenol [e.g., Triton X-114 (Rohm & Haas Co.)]; and (c) about 15% α -emulsan by weight in combination with an ethoxylated alkyl phenol having an R group of about 8 or 9 carbon atoms [e.g., Tergitol NP-40 (Union Carbide Corp.)]. A particularly preferred surfactant package comprises about 10% to about 20% α -emulsan by weight in combination with a nonionic ethoxylated alkyl phenol [e.g., Tergitol NP-40] and an anionic ethoxylated alcohol sulfate [e.g., Alfonic 1412-A (Conoco, Inc.)], using the nonionic and anionic surfactants in a proportion of about 1:1. The particularly preferred surfactant packages are exemplified by the surfactant package comprising about 15% by weight α -emulsan, about 42.5% by weight Tergitol NP-40 and about 42.5% by weight Alfonic 1412-A. Surfactant packages may be formulated full strength or in diluted aqueous solution. The surfactant package most preferred for use with viscous residuals is a combination of anionic surfactants, 85% by weight of an ethoxylated sulfated

nonylphenol, and 15% by weight of the sodium salt of a polymerized alkylnaphthalene sulfonic acid with a molecular weight of at least about 500 daltons and preferably at least about 2000 daltons.

6.2. Viscous Crude Oils and Residual Oils

The surfactant package compositions of this invention can be used to emulsify or emulsify and substantially stabilize numerous viscous hydrocarbons in oil-in-water emulsions which may be subsequently transported and/or directly burned. As there is no universally accepted, precise definition of the viscous hydrocarbons suitable for use in this invention, they are best described in terms of their general characteristics. Viscous hydrocarbons encompass naturally-occurring viscous crude oils (also called heavy crude oils) as well as residual bottom-of-the-barrel products from refineries, such as vacuum resid, other residual fuel oils and asphalt. [See Section 4, Nomenclature, supra.] While low gravity does not necessarily coincide with high density, these characteristics are generally correlated in viscous hydrocarbons.

Generally, the following characteristics are considered typical of the types of crude oils and residual oils, the handling and utilization of which can be facilitated by the compositions and methods of this invention:

1. Low API gravity, generally at or below about 20° API. This is the most frequently used criterion, both because it is easily measured and because 20° API crude roughly corresponds to the lower limit recoverable with conventional production techniques.
2. Viscosities in the range of about 10² to 10⁶ centipoise (cp) or even higher in some cases.
3. High metal contents. For example, heavy crudes often have nickel and vanadium contents as high as 500 ppm.
4. High sulfur content, e.g., 3 weight percent or more.
5. High asphaltene content.
6. High pour point.

It is to be noted, of course, that lighter crudes may also be emulsified and/or stabilized with the surfactant packages of this invention. However, since the transportation and combustion of light oils do not present the same problem as highly viscous crudes and residuals, the compositions and methods of this invention are more particularly directed to the use of heavy materials. Nevertheless, it may be useful to form pre-atomized fuels out of these light oils for emissions reductions purposes. Those viscous hydrocarbons which can be emulsified with the surfactant packages of this invention and which are most useful to emulsify for transportation and/or burning purposes can be generally defined as having a paraffin content of about 50% by weight or less and an aromatic content of about 15% by weight or greater with viscosities of about 100 centipoise or greater at 150° F. The viscous residuals generally are characterized by a paraffin content in the range from about 4% to about 40% by weight, an aromatic content in the range from about 15% to about 70% by weight and an asphaltene content from about 5% to about 80% by weight.

More specifically, the types of crude oils that can be successfully emulsified and stabilized with the surfactant packages of this invention include Boscan (Venezuela) crude, an east Texas crude, Jibaro and Bartra (Peru) crudes, El Jobo (Venezuela) crude, and a Kansas crude. The specific viscous residuals that can be successfully emulsified and stabilized with surfactant packages of this invention include California vacuum resid, Oklahoma vacuum resid, German visbreaker resid, Texas visbreaker resid, catalytic hydrogenated resid, ROSE resid, and cutback tar.

Furthermore, residual fuel oils such as those classified as ASTM Grade Number 6 Oils can also be emulsified. Number 6 oils, sometimes referred to as "Bunker C" oils, are high-viscosity oils used mostly in commercial and industrial heating. Their utilization normally requires preheating in the storage tank to permit pumping, and additional preheating at the burner to permit atomizing. The extra equipment and maintenance required to handle Number 6 fuels in nonemulsified form usually precludes its use in small installations. The ASTM standard specifications for Number 6 fuel oils are summarized in Table VI ["Standard Specification for Fuel Oils," ASTM Designation D396-80, in: 1981 Book of ASTM Standards, Part 23].

TABLE VI
DETAILED REQUIREMENTS FOR
NUMBER 6 FUEL OILS

	Grade of Fuel Oil (No. 6, Preheating Required for Burning and Handling)	
	Minimum	Maximum
Flash Point, °C. (°F.)	60 (140)	
Water and Sediment, Vol %	2.00 ²	
Saybolt Viscosity, s ¹ Universal at 38° C. (100° F.)	(> 900)	(9000)
Fuel at 50° C. (122° F.)	(> 45)	(300)
Kinematic Viscosity, cSt ¹ At 50° C. (122° F.)	> 92	638

¹Viscosity values in parentheses are for information only and not necessarily limiting.
²The amount of water by distillation plus the sediment by extraction shall not exceed 2.00%. The amount of sediment by extraction shall not exceed 0.50%. A deduction in quantity shall be made for all water and sediment in excess of 1.0%.

6.3. Emulsion Formation

The surfactant packages of Section 6.1 can be used to form oil-in-water emulsions containing as much as about 90% by volume of the viscous hydrocarbons described in Section 6.2. The aqueous phase into which they hydrocarbon is emulsified can be deionized water, water from a municipal source, or any water, even water with relatively large amounts of dissolved solids such as connate waters or brines, normally located in proximity to oil production, transportation or utilization sites. The aqueous phase can also be an alcohol/water mixture such as methanol/water, ethanol/water or other lower alkanol/water mixtures, and may further contain additives such as anti-corrosion agents, anti-pollution agents or combustion improvers. Oil-in-water emulsions preferably contain oil/water ratios of about

60/40 to about 80/20, and more preferably from about 65/35 to about 75/25.

Informing oil-in-water emulsions, it is economically desirable to use as little of the surfactant package as possible while maintaining acceptable emulsion characteristics to suit the particular transportation or utilization requirements. The surfactant packages of Section 6.1 can be used in proportions of surfactant package:hydrocarbon from about 1:100 to about 1:20,000 by weight. The proportion used can depend on the type of hydrocarbon to be emulsified and/or the purpose for emulsifying it.

Oil-in-water emulsion formation can be brought about by any number of suitable procedures. For example, the aqueous phase containing an effective amount of surfactant package can be contacted with the hydrocarbon phase by metered injection just prior to a suitable mixing device. Metering is preferably maintained such that the desired hydrocarbon/water ratio remains relatively constant. Mixing devices such as pump assemblies or in-line static mixers can be used to provide sufficient agitation to cause emulsification. As a more specific example, for the transportation or utilization of residual oils, it may be possible to emulsify the hot residual oil in about 30% aqueous phase (v/v) with one of

the surfactant packages of Section 6.1 as it exits the vacuum still of a refinery.

6.3.1. FORMATION OF PRE-ATOMIZED FUELS AT HIGH TEMPERATURES

Some low gravity residual hydrocarbons are extremely viscous and require very high temperatures to make them fluid enough to handle. Such hydrocarbons can be characterized by a viscosity greater than about 1000 cp at 212° F. Maintaining such high temperatures is not economically feasible for the long term storage and transportation of these hydrocarbons. Also, it is not economically feasible to blend these viscous hydrocarbons with much lighter oils (cutter stock) due to either the quantity of lighter oil required to achieve a viscosity which can be handled or the unfavorable characteristics of the viscous hydrocarbon which do not allow for homogeneous blending of lighter oils.

This invention offers a novel approach to handling extremely viscous hydrocarbons by the stable dispersion of such viscous hydrocarbons into water to form pre-atomized fuels. Pre-atomized fuel formation is achieved by heating the viscous hydrocarbon to a high temperature in order to make it fluid. The hot hydrocarbon phase is brought in contact with the aqueous phase containing appropriate surfactants and/or stabilizers as described in Section 6.1. A key to achieving successful pre-atomized fuel formation is the maintenance of pressure throughout the entire process such that the aqueous phase is not allowed to vaporize. By maintaining the appropriate pressure, i.e., the pressure required to prevent the water in the aqueous phase from boiling, the aqueous phase remains in a liquid state, thus allowing the stable dispersion of the hydrocarbon phase into a continuous water phase. The resulting hot pre-atomized fuel may be rapidly cooled using an appropriate heat exchange device so that the outlet temperature of the pre-atomized fuel is below the vaporization temperature of the aqueous phase at ambient pressure. Alternatively, the pressure may be reduced and the mixture cooled by flashing a portion of the water contained in the pre-atomized fuel.

6.3.2. Formation of Pre-Atomized Fuels Using A Thermally Cracked Hydrocarbon Discharge

As is generally known in the refining industry, residual hydrocarbons obtained from the discharge of thermal cracking units have presented unusual problems. The extreme conditions required in processing to obtain greater quantities of high gravity hydrocarbons have resulted in resids which are very susceptible to separation into distinct, non-mixable fractions. The reasons for the occurrence of this phenomenon are not fully known; however, it is believed that the destabilization of high molecular weight components such as asphaltene is a contributing factor. When such hydrocarbons are used to form pre-atomized fuels as described in Section 6.3., the resulting oil-in-water emulsion may separate into three phases after a short period of static storage. These phases consist of a low API gravity hydrocarbon bottom phase, a water/surfactant middle phase, and a high API gravity hydrocarbon upper phase. Without wishing to be bound or restricted by any particular theory, applicants theorize that the separation may be due to the slow cooling of the pre-atomized fuel which allows sufficient time for the occurrence of complex interactions that may be attributed to both "sticky state" and Ostwald ripening phenomena. The tendency toward separation can be decreased by the use of an appropriate heat exchange device or method to rapidly quench the fresh formed pre-atomized fuel to a temperature at least about 100° F. below the softening point of the hydrocarbon. By rapidly quenching the oil-in-water emulsion as it exits the mixing unit, a stable pre-atomized fuel is achieved that does not separate with time. It is further theorized that the rapid cooling of the hot pre-atomized fuel does not allow sufficient time for the complex interactions stated above to occur.

6.3.3. Mixing of a slurry with a pre-atomized fuel

An economical way to increase the btu content of a liquid fuel is achieved by incorporating a high softening

point hydrocarbonaceous material (such as coal, coke, ROSE residual, etc.) into a lower softening point fuel. This is usually accomplished by grinding a high softening point hydrocarbon to form very small particles (usually approximately 100 μm in size) and then, dispersing the solid particles in the liquid fuel. The dispersion of a solid in a liquid, however, usually results in the production of a fuel with unfavorable characteristics such as increased viscosity.

A novel method of economically utilizing a high softening point hydrocarbonaceous material (such as coal, coke, ROSE residual, etc.) is achieved by incorporating it into a pre-atomized fuel. This is accomplished by first grinding a material of high softening point to form very small particles (generally less than about 30 μm) and then forming a slurry by dispersing the particles in a continuous aqueous phase containing a pre-atomized fuel-compatible surfactant package.

The slurry of dispersed particles is mixed at an appropriate ratio with a pre-atomized fuel formulated from a hydrocarbon other than that used to form the slurry. The mixing of a slurry with a pre-atomized fuel results in a liquid fuel which has a viscosity lower than either the slurry or the pre-atomized fuel prior to mixing. The reasons for the reduced viscosity observed in a slurry/pre-atomized fuel mixture are not fully known; however, without wishing to be bound or restricted by any particular theory, applicants believe that the reduction of particle-to-particle interaction is a contributing factor.

6.4. Properties of Emulsion-Stabilized Hydrocarbons

The hydrocarbon droplets of hydrocarbon-in-water emulsions generally rise to the surface and "float" on the aqueous phase in a process known as creaming, provided the density of the hydrocarbon phase is less than that of the aqueous phase and the droplets in the dispersed phase are too big to be stabilized by Brownian motion. If the "cream" remains undisturbed for a given period of time, the droplets coalesce, giving rise to two separate phases. The emulsions, particularly α -emulsions, are extremely effective in retarding coalescence and the emulsion-stabilized droplets in the "cream" are easily redispersible in the aqueous phase.

The principal factors controlling emulsion stability are electrostatic (charge) effects and steric effects. The properties of emulsions lend themselves to optimal exploitation of these mechanisms. Their large molecular weight and highly specific three-dimensional structure result in an efficient coverage of the hydrocarbon/water interface. This effectively prevents oil-to-oil contact when collisions occur between adjacent droplets. Simultaneously, the polyanionic nature of emulsions causes the surfaces of emulsion droplets to be negatively charged which creates repulsive forces and significantly decreases the collision frequency between hydrocarbon droplets. In addition, the absence of multimolecular emulsion micelles in the water phase and the lack of emulsion solubility in the hydrocarbon phase provides an efficient migration and attachment of the emulsion molecules to the oil/water interface. The overall chemi-

cal requirements for emulsion stabilization thus become very small and directly related to the oil droplet size, i.e., interfacial area desired.

The advantages that emulsans offer over classical emulsion stabilizers may be summarized as follows. In a hydrocarbosal, emulsan predominantly resides at the oil/water interface only; essentially no measurable emulsan is found in the water phase nor in the oil phase. Very small amounts of emulsan are required, even in the presence of excess water. The emulsan-stabilized hydrocarbosal effectively resists inversion to water-in-oil emulsions, even at water:oil ratios of less than about 1:4. This is partly due to emulsans' insolubility in oil and may also be due in part to the specific three-dimensional structure of the emulsan molecule.

6.5. Blending of Hydrocarbons

In some cases hydrocarbons may be too viscous for conventional processing or have characteristics (i.e., low gravity; excessive paraffinic, aromatic, and/or asphaltic contents; etc.) which make them unfavorable to incorporate into stable pre-atomized fuels. One method to reduce viscosity for processing or alleviate unfavorable characteristics is blending the unfavorable hydrocarbon with one which is favorable resulting in a hydrocarbon having characteristics suitable for pre-atomized fuel formation. In this way an otherwise unusable hydrocarbon can be "adjusted" to a usable form.

6.6. Transportation and Utilization of Hydrocarbosals

Hydrocarbosals, because they contain bioemulsifiers, have properties which allow them to be transported in tankers, barges and more importantly through conventional pipelines, including standard, non-heated pipeline networks. Among the properties exhibited by hydrocarbosals that are particularly important for pipelining are reduced viscosity, stabilization against coalescence even under considerable rates of shear, compatible formation with high-salinity aqueous phases, and non-corrosive nature. Hydrocarbosals with viscosities below about 500 cp at about 60° F. allow the economical use of centrifugal pumps for transportation of oil at acceptable flow rates and reasonable pressure drops. For pipelining purposes, it is desirable to use the surfactant packages of Section 6.1 at their minimum effective concentrations which frequently are in a proportion within the range of about 1:100 to about 1:5,000. Hydrocarbosals may be stored in non-heated storage tanks where agitation may be optionally supplied to maintain homogeneity.

Once transported to their destination, hydrocarbosals can be demulsified if desired. More importantly, hydrocarbosals like other pre-atomized fuels can be utilized directly, without dewatering, as burnable fuels. They can be used in combustion facilities which presently use Number 6 fuel oils, or so-called Bunker C oils, to fire, inter alia, steam generators, heating systems or blast furnaces. Hydrocarbosals, as is the case with other preatomized fuels, may potentially allow for less expensive plant operation by reducing fuel costs, storage costs and material handling costs. Hydrocarbosals and other preatomized fuels may have applications as substitutes

for Number 2 or higher grade fuels depending on the situation.

Where long storage periods or transportation over long distances prior to utilization is not required, the stability exhibited by hydrocarbosals becomes less critical. If short distance-transportation or on-site utilization is contemplated, it may not be necessary to form bioemulsifier-stabilized emulsions. Further, it is not necessary to form stabilized emulsions in order to facilitate combustion; i.e., emulsion stability is not generally required for good combustion characteristics. Therefore, pre-atomized fuels suitable for burning can be made by emulsifying viscous hydrocarbons with the surfactant packages of Section 6.1 which are formulated with a chemical surfactant alone or a combination of chemical surfactants. For instance, a 70/30, Number 6 fuel oil/water emulsion can be made with a surfactant package comprising a nonionic chemical surfactant and an anionic chemical surfactant in equal proportion by weight and the resulting oil-in-water emulsion (which can also be referred to as a pre-atomized fuel) can be burned directly.

7. EXAMPLES

7.1. Preparation of Bioemulsifiers

7.1.1. Preparation of technical grade α -emulsan

The α -emulsans produced by *Acinetobacter calcoaceticus* ATCC 31012 during fermentation on ethanol are known bioemulsifiers as described in U.S. Pat. No. 4,395,354, incorporated by reference supra. The α -emulsans used in the experiments described infra were technical grade materials (unless otherwise indicated) which were prepared in either of two ways. Both methods of preparation involved enzyme treatment and drying but differed in the order in which these steps were performed. By one method, centrifuged (approximately 90% cell-free) fermentation broth containing α -emulsans resulting from a fermentation of *Acinetobacter calcoaceticus* ATCC 31012 in ethanol medium was drum-dried and the resulting material was treated in the following manner prior to use. A 10% by weight suspension of the material, so-called technical grade α -emulsan, was prepared in deionized water and heated to 50°-60° C. while continuously stirring. The pH of the suspension was adjusted to pH 8.5 by adding 50% by weight sodium hydroxide (diluted, if necessary). Protease enzyme (NOVO Industries, 1.5M Alcalase) was added at a level of 1 part protease:500 parts solid α -emulsan. The mixture was allowed to remain at 50°-60° C. while being stirred for about three hours. Reactions were run to completion as judged by the absence of visible precipitable emulsan following centrifugation of the reaction mixture. After completion of the enzyme treatment, the reaction mixtures were raised to approximately 70° C. to denature the protease and stop its activity. The solutions were cooled to room temperature and Cosan PMA-30 (Cosan Corporation), a preservative, was added at a level of 1 part Cosan:500 parts α -emulsan solution.

By another method, enzyme treatment of the α -emulsan was performed prior to drum drying according to

the following protocol. Fermentation broth containing α -emulsan resulting from a fermentation of *Acinetobacter calcoaceticus* ATCC 31012 in ethanol medium was centrifuged to remove approximately 90% of the bacterial cells. To the centrifuged broth, protease enzyme (as previously described) was added in a ratio of 1 gram protease:500 units per milligram of Specific Emulsification Activity (where one unit per milligram of Specific Emulsification Activity is defined as that amount of emulsifying activity per milligram of bioemulsifier which yields 100 Klett absorption units using a standard hydrocarbon mixture consisting of 0.1 ml of 1:1 (v/v) hexadecane/2-methylnaphthalene and 7.5 ml of Tris-Magnesium buffer). The protease reaction was run to completion as described supra. The protease-treated centrifuged broth was then evaporated to a 10% (w/v) slurry of α -emulsan. The slurry was sprayed dried and the resulting material is also referred to as technical grade α -emulsan.

7.1.2. Additional preparations of acinetobacter calcoaceticus bioemulsifiers

Fermentations of *Acinetobacter calcoaceticus* ATCC 31012 were run on ethanol as described in U.S. Pat. No. 4,395,354. The following fractions of the resulting broth were used to formulate surfactant packages: whole broth, supernatants, cells, enzyme-treated whole broth, enzymetreated supernatants, enzyme-treated cells (where the enzyme treatment was as described for the second method in Section 7.1.1. supra), homogenized cells, boiled cells, and so-called "Millipore emulsan." Millipore emulsan is prepared by Millipore filtering whole broth to remove cells, followed by enzyme treatment (described supra) and ultrafiltration. The foregoing preparations were used in liquid or wet form. The Millipore emulsan samples can be further dialyzed against ammonium bicarbonate and freeze-dried prior to use in surfactant packages.

Whole broth and enzyme-treated whole broth from fermentations of *Acinetobacter calcoaceticus* ATCC 31012 on soap stock (run under conditions similar to those described in U.S. Pat. No. 4,230,801, incorporated by reference, supra) were also used.

Acinetobacter calcoaceticus NS-1 (NRRL B-15847) was grown in a fermentor on ethanol medium under conditions similar to those described in U.S. Pat. No. 4,395,354. Both whole broth and enzyme-treated whole broth were used to formulate surfactant packages.

Acinetobacter calcoaceticus strains NS-4 (NRRL B-15848), NS-5 (NRRL B-15849), NS-6 (NRRL B-15860) and NS-7 (NRRL B-15850) were grown for 3 days in shake flask cultures in 2% ethanol medium as described in U.S. Pat. No. 4,395,354. Enzyme-treated whole broth samples were prepared from the NS-4, NS-5 and NS-7 cultures. Enzyme-treated supernatant samples were prepared from NS-4, NS-5, NS-6 and NS-7 cultures. These preparations were also used to formulate surfactant packages.

7.2. Viscous Hydrocarbon Characteristics

7.2.1. Boscan crude oil

The Boscan crude oil used in the experiments described infra was a heavy crude produced from the oilfields of western Venezuela. The characteristics of

the crude, its specific gravity, API gravity ($^{\circ}$ API), paraffin content (% by weight), aromatic content (% by weight), asphaltene content (% by weight) and viscosity (in centipoise) versus temperature (degrees Fahrenheit) profile, were determined experimentally and are summarized in Table VII. The paraffin, aromatic and asphaltene content were determined by the methods described in Section 7.2.12, infra.

TABLE VII

BOSCAN CRUDE OIL CHARACTERISTICS	
Specific Gravity =	0.983
API Gravity (calculated) =	12.5 $^{\circ}$ API
Paraffin content =	18.0% (w/w)
Aromatic content =	60.0% (w/w)
Asphaltene content =	22.0% (w/w)
Viscosity (cp)	Temperature ($^{\circ}$ F.)
4,300	140
24,000	100
192,000	60

7.2.2. Texas fireflood crude oil

The Texas crude oil used in the experiments described infra was produced from an oilfield in east Texas (Quitman, TX) by the fireflood method. The characteristics of the crude, its specific gravity at 26 $^{\circ}$ C. [ASTM D1217-81], API gravity, paraffin content, aromatic content and viscosity versus temperature profile, were determined experimentally as described in Section 7.2.11, infra, and are summarized in Table VIII.

TABLE VIII

TEXAS FIREFLOOD CRUDE OIL CHARACTERISTICS	
Specific Gravity =	0.981
API Gravity (calculated) =	12.7 $^{\circ}$ API
Paraffin content =	26.1% (w/w)
Aromatic content =	51.1% (w/w)
Viscosity (cp)	Temperature ($^{\circ}$ F.)
1,748	160
4,085	140
8,752	120
27,615	100
62,000	80

7.2.3. Number 6 residual test fuel oil

The Number 6 residual fuel oil used in the experiment described in Section 7.5 was obtained from the MIT Energy Laboratory (Cambridge, Mass.). The characteristics of this residual fuel oil, its specific gravity, API gravity, paraffin content, aromatic content, asphaltene content and viscosity versus temperature profile, were determined experimentally and are summarized in Table IX. The paraffin, aromatic and asphaltene content were determined by the methods described in Section 7.2.12, infra.

TABLE IX

RESIDUAL NO. 6 TEST FUEL OIL CHARACTERISTICS	
Specific Gravity =	0.977
API Gravity (calculated) =	13.3 $^{\circ}$ API
Paraffin content =	23% (w/w)
Aromatic content =	38% (w/w)
Asphaltene content =	39% (w/w)
Viscosity (cp)	Temperature ($^{\circ}$ F.)
1,200	100
5,000	70

TABLE IX-continued

RESIDUAL NO. 6 TEST FUEL OIL CHARACTERISTICS	
20,000	40

7.2.4. Union cutback tar

The Union cutback tar used in the experiments described infra was a California resid which had been mixed with cutter stock to facilitate handling. The characteristics of this tar, its specific gravity, API gravity, paraffin content, aromatic content, asphaltene content, ash content and viscosity versus temperature profile were determined experimentally and are summarized in Table X. The paraffin, aromatic and asphaltene content were determined by the methods described in Section 7.2.12, infra.

TABLE X

UNION CUTBACK TAR CHARACTERISTICS	
Specific Gravity =	0.98
API Gravity (calculated) =	12.9° API
Paraffin content =	22% (w/w)
Aromatic content =	54% (w/w)
Asphaltene content =	24% (w/w)
Ash content =	7% (w/w)
Viscosity (cp)	Temperature (°F.)
1,796	210
4,490	190
12,347	170
123,479	130

7.2.5. California vacuum resid

The California Vacuum Resid used in the experiments described infra was a vacuum bottom obtained from a Kern County crude oil and provided by a California refinery. The characteristics of this residual oil, its specific gravity, API gravity, paraffin content, aromatic content, asphaltene content, and viscosity versus temperature profile were determined experimentally and are summarized in Table XI. The paraffin, aromatic and asphaltene content were determined by the methods described in Section 7.2.12, infra.

TABLE XI

CALIFORNIA VACUUM RESID CHARACTERISTICS	
Specific Gravity =	.9934
API Gravity (calculated) =	10.9° API
Paraffin content =	17% (w/w)
Aromatic content =	72% (w/w)
Asphaltene content =	11% (w/w)
Viscosity (cp)	Temperature (°F.)
4,490	220
27,838	180
206,540	140

7.2.6. Oklahoma vacuum resid

The Oklahoma vacuum resid used in the experiments described infra was a vacuum bottom obtained from a mid continent refinery. The characteristics of this residual oil, its specific gravity, API gravity, paraffin content, aromatic content, asphaltene content, and viscosity versus temperature profile were determined experimentally and are summarized in Table XII. The paraffin, aromatic and asphaltene content were determined by the methods described in Section 7.2.12, infra.

TABLE XII

OKLAHOMA VACUUM RESID CHARACTERISTICS	
Specific Gravity =	.9364
API Gravity (calculated) =	19.6° API
Paraffin content =	20% (w/w)
Aromatic content =	70% (w/w)
Asphaltene content =	10% (w/w)
Viscosity (cp)	Temperature (°F.)
3,098	220
14,143	180
98,780	140
251,440	120

7.2.7. CATALYTIC HYDROGENATED RESID (H-OIL)

The H-oil used in the experiments described infra was obtained by a process in which residual oil is catalytically hydrogenated. This resid was from a refinery in Louisiana. The characteristics of this residual oil, its specific gravity, API gravity, paraffin content, aromatic content, asphaltene content, and viscosity versus temperature profile were determined experimentally and are summarized in Table XIII. The paraffin, aromatic and asphaltene content were determined by the methods described in Section 7.2.12, infra.

TABLE XIII

H-OIL CHARACTERISTICS	
Specific Gravity =	1.0196
API Gravity (calculated) =	7.3° API
Paraffin content =	22% (w/w)
Aromatic content =	57% (w/w)
Asphaltene content =	21% (w/w)
Viscosity (cp)	Temperature (°F.)
2,424	20
19,936	160
244,705	120

7.2.8. Rose resid

The ROSE resid used in the experiments described infra was obtained by the ROSE (Residuum Oil Supercritical Extraction) process which extracts remaining light fractions from vacuum bottoms. The characteristics of this residual oil, its specific gravity, API gravity, paraffin content, aromatic content, asphaltene content, and viscosity versus temperature profile were determined experimentally and are summarized in Table XIV. The paraffin, aromatic and asphaltene content were determined by the methods described in Section 7.2.12, infra.

TABLE XIV

ROSE RESID CHARACTERISTICS	
Specific Gravity =	1.17
API Gravity (calculated) =	-10.6° API
Paraffin content =	4% (w/w)
Aromatic content =	18% (w/w)
Asphaltene content =	78% (w/w)

7.2.9. German visbreaker resid

The German visbreaker used in the experiments described infra was obtained by thermal cracking of vacuum bottoms. The visbreaker resid was from a refinery located in the Federal Republic of Germany. The characteristics of this residual oil, its specific gravity, API gravity, paraffin content, aromatic content, asphaltene content, and viscosity versus temperature profile were

determined experimentally and are summarized in Table XV. The paraffin, aromatic and asphaltene content were determined by the methods described in Section 7.2.12, infra.

TABLE XV

GERMAN VISBREAKER RESID CHARACTERISTICS	
Specific Gravity =	0.953
API Gravity (calculated) =	16.6° API
Paraffin content =	17% (w/w)
Aromatic content =	61% (w/w)
Asphaltene content =	22% (w/w)
Viscosity (cp)	Temperature (°F.)
2,470	200
16,389	160
174,032	120

7.2.10. Texas visbreaker resid

The Texas visbreaker used in the experiments described infra was obtained by thermal cracking of vacuum bottoms. The visbreaker resid was from a refinery located in Texas. The characteristics of this residual oil, its specific gravity, API gravity, paraffin content, aromatic content, asphaltene content, and viscosity versus temperature profile were determined experimentally and are summarized in Table XVI. The paraffin, aromatic and asphaltene content were determined by the methods described in Section 7.2.12, infra.

TABLE XVI

TEXAS VISBREAKER RESID CHARACTERISTICS	
Specific Gravity =	0.989
API Gravity (calculated) =	11.6° API
Paraffin content =	28% (w/w)
Aromatic content =	48% (w/w)
Asphaltene content =	24% (w/w)
Viscosity (cp)	Temperature (°F.)
449	200
898	160
4,624	120
61,782	80

7.2.11. Methods for determining hydrocarbon characteristics

Viscosity versus temperature profiles were obtained by heating the oils to the given temperatures of Tables VII-XIII and XV-XVI and measuring viscosities in a Rheomat 30 rheometer (Contraves AG), at an approximate shear rate of 30 sec.⁻¹.

The paraffin content and aromatic content of some of the oils of the foregoing examples were determined by a method in which the oil is separated into fractions based on hydrocarbon solubilities in n-heptane and methylene chloride. The paraffin fraction is defined as that hydrocarbon fraction which is soluble in n-heptane. The aromatic fraction is defined as that hydrocarbon fraction which is soluble in methylene chloride.

The materials used are as follows: an analytical balance, accurate to 0.1 milligram (mg), a 500 millimeter (mm) burette-type chromatography column, tared collection flasks, reagent grade methylene chloride, n-heptane (99 mole percent) and alumina adsorbent. The alumina was activated by heating it in an oven set at 310° C. for 12-14 hours. The alumina was cooled in a

dessicator and stored in a tightly capped bottle prior to use. Chromatography columns packed $\frac{1}{8}$ full were used.

The separation was carried out by quantitatively weighing 500 to 1000 mg (± 0.1 mg) of sample oil. Viscous oils were weighed into sample pouches made of tissue paper which were subsequently placed into the column. (Non-viscous oils are usually weighed directly into the columns.) After introduction of the sample oil into the columns, 200 to 250 ml of n-heptane were allowed to flow through the column. It was preferable for the solvent to be added in a manner which did not excessively disturb the alumina packing. The eluent was collected in a tared evaporating flask. After all the n-heptane had flowed through the column, the first evaporating flask was replaced with another tared flask. Methylene chloride was then introduced into the column and allowed to flow through it.

The collected eluents were removed from each flask by vacuum evaporation following appropriate safety precautions. The dry flasks were reweighed and the percentage of paraffins and aromatics were calculated based on the original weight of the oil sample. All samples were run in duplicate.

Specific gravity was determined by weighing a measured volume of sample oil and calculating the ratio of the mass of the oil to the mass of an equal volume of water. API gravities were then calculated from the specific gravity by the general formula:

$$^{\circ}\text{API} = \frac{141.5}{\text{specific gravity at } 60/60^{\circ}\text{F.}} - 131.5.$$

7.2.12. Methods for determining hydrocarbon characteristics, including asphaltene content

The methods used to characterize the hydrocarbons of Examples 7.2.1, 7.2.3 through 7.2.10 are essentially the same as those in Section 7.2.11. However, a new procedure was utilized for determining the asphaltic in addition to the paraffinic and aromatic contents of viscous hydrocarbons. It is described below.

The paraffin, asphaltene and aromatic contents of the sample hydrocarbons were obtained by a method in which the hydrocarbons are dispersed in n-heptane, the asphaltenes removed by filtration and the remaining components separated based on their solubilities in n-heptane and methylene chloride. The asphaltene fraction (the precipitate) is filtered from a dispersion of the hydrocarbon in n-heptane. The paraffin fraction is that portion soluble in n-heptane. The aromatic fraction is that portion soluble in methylene chloride.

The materials used are as follows: an analytical balance, accurate to 0.1 milligram (mg), a blender (Osterizer Galaxy 14) and blades fitted to a 500 ml Mason jar, preweighed Whatman #1 paper, filter funnel, rotary evaporation apparatus, a 500 millimeter (mm) burette-type chromatography column, tared collection flasks, reagent grade methylene chloride, n-heptane (99 mole percent) and alumina adsorbent. The alumina was activated by heating it in an oven at 310° C. for 12-14 hours. The alumina was cooled in a dessicator and

stored in a tightly capped bottle prior to use. Chromatography columns packed $\frac{1}{8}$ full were used.

Hydrocarbon samples of 1-2 g were quantitatively added to Mason jars containing 100 ml of n-heptane. After blending for 1-2 minutes at maximum speed, the jar and its contents were washed with an additional 100 ml of n-heptane. The dispersed sample was filtered through Whatman #1 paper and the filtrate collected into Erlenmeyer flasks. After introduction of the filtrate to the column, the effluent was collected into a tared evaporation flask. When n-heptane was completely eluted, 200 ml of methylene chloride was added to the column and the eluted material collected into another tared evaporation flask until the column ran dry.

The eluting solvents were removed using a rotating vacuum evaporator at temperatures appropriate to the solvents.

The tared filter paper and flasks were reweighed and the percentage of asphaltene, paraffins, and aromatics were calculated based on the original weight of the sample. Individual samples were run in duplicate. All percentages appearing in the foregoing tables for paraffinic, aromatic and asphaltene content have been adjusted to 100% recovery for comparative purposes.

7.3. Viscosity Reduction Experiments

7.3.1. Surfactant Packages and Emulsification of Hydrocarbons

The compositions of five surfactant packages which have been used successfully to emulsify Boscan crude oil are presented in Table XVII. The α -emulsan used was a technical grade α -emulsan prepared according to the first method described in Section 7.1.1. The chemical surfactants, Tergitol 15-S-X (where X indicates the number of moles of ethylene oxide), Tergitol TMN-6, Tergitol NP-40 (Union Carbide Corp.), Triton X-114 (Rohm & Haas Co.) and Alfonic 1412-A (Conoco) are commercially available. Emulsions were formed in an Osterizer Galaxy 14 blender at low speed in a manner preventing the beating of air into the emulsion. The ratio of Boscan crude to deionized water was 70:30 by volume (v/v). The surfactant packages were used successfully over a range of 1:250-1:2,000 [surfactant package:oil, by weight (w/w)]. The surfactant package comprising 15% α -emulsan, 42.5% Tergitol NP-40 and 42.5% Alfonic 1412-A was considered a preferred surfactant package for use with Boscan crude oil. Emulsions (70/30, Boscan crude/deionized water) formed with this surfactant package at 1 part per 2,000 parts oil have been observed to be stable and maintain reduced viscosities for a period of at least three weeks. In addition, this surfactant package has been used to form

70/30 Boscan crude/water emulsions at as low a treatment rate as 1 part per 20,000 parts oil.

TABLE XVII

SURFACTANT PACKAGES FOR EMULSIFYING BOSCAN CRUDE

Package # Component	% of Component (w/w) in Surfactant Package				
	1	2	3	4	5
α -Emulsan	10	13	—	15	15
Tergitol 15-S-X	90	—	—	—	—
Tergitol TMN-6	—	22	—	—	—
Tergitol NP-40	—	—	100	85	42.5
Triton X-114	—	65	—	—	—
Alfonic 1412-A	—	—	—	—	42.5

Other surfactants which successfully [alone or in combination] emulsified general type viscous oils included Alfonic 1012-60 (Conoco, Inc.), an ethoxylated linear alcohol with chain lengths of 10 to 12 carbon atoms (C₁₀-C₁₂) and 60% ethoxylation; Protowet 4196 (Proctor Chemical Co.), a sodium salt of a sulfosuccinate of a nonyl phenol ethoxylate; Protowet 4337 (Proctor Chemical Co.), sodium dicyclohexyl sulfosuccinate; Tween 80 (ICI Americas, Inc.), polyoxyethylene (20) sorbitan monooleate; Pluronic F88 (BASF Wyandotte), a block copolymer of propylene oxide and ethylene oxide; Petronate L (Witco Chemical Corp.) a sodium petroleum sulfonate; and Conoco AXS (Conoco, Inc.), ammonium xylene sulfonate.

The compositions of several surfactant packages which have been successfully used to emulsify Oklahoma vacuum resid are listed in Table XVIII. The α -emulsan used was prepared from a whole broth of emulsan according to the methods described in Section 7.1.2. The surfactants, Tetronic 7007 (BASF Wyandotte Corp.), Alipal EP-110, CO-436 (GAF Cor.), Daxad 17 (W. R. Grace & Co.), Nopcosant (Diamond Shamrock), Triton X series and Tamol 850 (Rohm & Haas Co.), Tergitol NP series (Union Carbide Corp.) and Conoco Sulfate 219 (Continental Chemical Co.) are commercially available. Emulsions were formed in an Osterizer Galaxy 14 blender at medium speed in a manner preventing the beating of air into the emulsion. The ratio of the Oklahoma vacuum resid to tap water was 70:30 by weight (w/w). The surfactant packages were used successfully over a range of 1:10 to 1:250 (surfactant package:oil) by weight (w/w). The surfactant package comprising 15% Daxad 17 and 85% Alipal CO-436 was considered a preferred surfactant package for use with Oklahoma vacuum resid. The emulsion produced with this package has been observed to be stable and maintain a reduced viscosity for at least 5 weeks. This formulation has been used to form a 70/30 resid/water emulsion at a treatment as low as 1 part to 750 parts of oil.

TABLE XVIII

SURFACTANT PACKAGES FOR PRE-ATOMIZED FUELS

Package # Component	% of component in package (w/w)													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
α -Emulsan:														
whole broth	15	15	15	15	15	15	—	—	—	—	—	—	—	17
technical	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tetronic 707	85	—	—	—	—	—	—	—	—	—	—	—	—	—
Alipal EP-110	—	85	—	—	—	—	100	—	—	—	—	—	—	—

TABLE XVIII-continued

SURFACTANT PACKAGES FOR PRE-ATOMIZED FUELS													
Alipal CO-436	—	—	85	—	—	—	—	100	—	—	—	—	
Tamol 850	—	—	—	—	—	—	—	—	—	—	—	—	
Daxad 17	—	—	—	—	—	—	—	100	—	—	—	—	
Nopcoasant	—	—	—	—	—	—	—	—	100	—	—	—	
Triton X-114	—	—	—	—	—	—	—	—	—	—	—	50	
Triton X-165	—	—	85	—	51	—	—	—	—	100	—	—	
Triton X-405	—	—	—	—	—	—	—	—	—	—	—	—	
Triton X-705	—	—	—	—	—	—	—	—	—	—	—	—	
Tergitol NP-6	—	—	—	28	11	—	—	—	—	—	—	—	
Tergitol NP-8	—	—	—	—	—	—	—	—	—	—	—	33	
Tergitol NP-40	—	—	—	37	23	—	—	—	—	—	100	—	
Tergitol NP-70	—	—	—	—	—	—	—	—	—	—	—	—	
Orzan A	—	—	—	—	—	—	—	—	—	—	—	—	
Lignosol BD	—	—	—	—	—	—	—	—	—	—	—	—	
Conoco Sulfate 219	—	—	—	—	—	—	—	—	—	—	—	—	
Package #	% of component in package (w/w)												
Component	15	16	17	18	19	20	21	22	23	24	25	26	27
<u>α-Emulsan:</u>													
whole broth	15	—	—	16.7	—	—	—	—	—	—	15	15	—
technical	—	14.2	14.2	—	—	—	—	—	—	—	—	—	—
Tetronic 707	—	—	—	—	—	—	—	—	—	—	—	—	—
Alipal EP-110	—	—	—	—	—	—	85	85	—	—	—	—	—
Alipal CO-436	—	—	—	—	85	85	—	—	—	—	—	—	85
Tamol 850	—	—	—	—	—	—	—	—	—	—	—	—	15
Daxad 17	—	—	—	—	15	—	15	—	15	—	—	—	—
Nopcoasant	—	—	—	—	—	—	—	—	—	—	—	—	—
Triton X-114	—	42.8	—	—	—	—	15	15	—	15	—	—	—
Triton X-165	—	—	—	—	—	—	—	—	—	—	—	—	—
Triton X-405	42.5	—	42.8	—	—	—	—	—	85	85	—	—	—
Triton X-705	—	—	—	50.0	—	—	—	—	—	—	—	—	—
Tergitol NP-6	—	—	—	—	—	—	—	—	—	—	—	—	—
Tergitol NP-8	—	28.6	—	—	—	—	—	—	—	—	—	—	—
Tergitol NP-40	42.5	—	28.6	—	—	—	—	—	—	—	—	—	—
Tergitol NP-70	—	—	—	33.3	—	—	—	—	—	—	85	—	—
Orzan A	—	—	—	—	—	—	—	—	—	—	—	—	—
Lignosol BD	—	14.2	14.2	—	—	—	—	—	—	—	—	—	—
Conoco Sulfate 219	—	—	—	—	—	—	—	—	—	—	—	85	—

The residual hydrocarbons described in Sections 7.2.4. through 7.2.10. were successfully emulsified into stable pre-atomized fuels with certain of the surfactant packages listed in Table XVIII. For the California and Oklahoma vacuum resids, the preferred surfactant package was Package #19. For the Union cutback tar, the preferred surfactant package was Package #25. Package #18 was preferred for use with the German visbreaker resid and Package #17 was preferred for the Texas visbreaker resid, the ROSE resid and the catalytically hydrogenated residual oil.

Table XIX lists the types of oils that have and have not yet been successfully emulsified into stable emulsions (see Section 3) with various surfactant packages. All the oils listed as having been successfully emulsified to form stable emulsions can be emulsified with a surfactant package comprising 15% α -emulsan (technical grade), 42.5% Tergitol NP-40, and 42.5% Alfonic 1412-A (weight percent) used at 1 part per 500 parts oil by weight. The method used for determining paraffin and aromatic content (weight percent) is described in Sections 7.2.11 and 7.2.12.

TABLE XIX
PARAFFIN/AROMATIC CONTENT AND
EMULSION STABILITY

Oil Type	Asphal- tene %	Paraf- fin %	Aro- matic %	Form Stable Emulsions*
Boscan Crude	22	18	60	yes
Uinta Crude	2	83	15	no

TABLE XIX-continued

PARAFFIN/AROMATIC CONTENT AND
EMULSION STABILITY

Oil Type	Asphal- tene %	Paraf- fin %	Aro- matic %	Form Stable Emulsions*
So. Calif. Fuel Oil	—	69	12	no
Texas Fireflood Crude	—	26	51	yes
Bombay Crude	—	75	8	no
Number 6 Residual Fuel Oil	39	23	38	yes
Jibaro Crude	—	19	64	yes
El Jobo Crude	—	13	52	yes
Kansas Crude	—	48	41	yes

*See Section 3 for description of stable emulsions.

7.3.2. Effect of methanol in aqueous phase on pre-atomized fuel viscosity

Pre-atomized fuels were formed in a blender at low speed (in a manner preventing the beating of air into the emulsion) with methanol incorporated into the aqueous phase. The hydrocarbon used was a mixture of Number 6 residual fuel oils, designated Amelia Fuel oil. The specific gravity of Amelia Fuel oil was 0.996 and its API gravity was 10.6° API. The viscosity versus temperature profile is shown in Table XX.

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TABLE XX

VISCOSITY VS. TEMPERATURE FOR AMELIA FUEL OIL	
Viscosity (cp)	Temperature (°F.)
1,046	100
1,405	90
2,190	80
3,578	70
6,209	60

The surfactant package comprised 15% α -emulsan (technical grade), 42.5% Tergitol NP-40 and 42.5% Alfonic 1412-A (w/w).

The surfactant package was added to aqueous phases containing various proportions of methanol and deionized water. The aqueous phases were blended at low speed for approximately 15 seconds to form pre-atomized fuels wherein the ratio of Amelia Fuel to aqueous phase was 70:30 (v/v). Enough of the surfactant package was added to the aqueous phase such that the final proportion of surfactant package to Amelia Fuel in the pre-atomized fuel was 1:250. Table XXI summarizes the variation of viscosity of the pre-atomized fuel as the composition of the aqueous phase was varied. The results suggest that addition of methanol up to at least about 45% does not significantly affect viscosity reduction by the surfactant package.

TABLE XXI

EFFECT OF METHANOL IN AQUEOUS PHASE ON VISCOSITY		
% ¹ Methanol	% ¹ Water	Viscosity (cp) ²
0	100.0	58.5
1.0	99.0	29.2
2.5	97.5	32.1
4.9	95.1	61.2
10.0	90.0	34.3
11.5	88.5	37.9
12.9	87.1	35.0
15.0	85.0	39.4
24.7	75.3	76.4
44.3	55.7	82.3
100.0	0	1753.7

¹Weight percent
²At 100° F.

7.3.3. Effect of water content on pre-atomized fuel viscosity

Experiments were performed with the Boscan crude oil described in Section 7.2.1, the Number 6 residual test fuel oil described in Section 7.2.3 and the Amelia Fuel oil described in Section 7.3.2 to determine the effect of variations in the proportion of the aqueous phase to oil phase on pre-atomized fuel viscosity. The surfactant package used in all three sets of experiments comprised 15% α -emulsan (technical grade), 42.5% Tergitol NP-40 and 42.5% Alfonic 1412-A (w/w). The viscosities reported in Tables XXII, XXIII and XXIV were measured on the Rheomat 30 as described in Section 7.2.11.

Boscan crude oil was emulsified at low speed in a blender (as in Section 7.3.1) in various proportions of water using a surfactant package ratio of 1:250 based on oil. Viscosities were measured at 100° F. The data are tabulated in Table XXII and presented graphically in FIG. 1.

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TABLE XXII

EFFECT OF WATER CONTENT ON VISCOSITY OF BOSCAN CRUDE OIL PRE-ATOMIZED FUELS	
Water Content, % (v/v)	Viscosity (cp) at 100° F.
24	202
27	140
30	111
33	82
35	51
39	36

Similarly, Number 6 residual test fuel oil was emulsified in various proportions of deionized water using a surfactant package ratio of 1:250 based on oil. Viscosities were measured at 100° F. The data are tabulated in Table XXIII.

TABLE XXIII

EFFECT OF WATER CONTENT ON VISCOSITY OF NUMBER 6 FUEL OIL PRE-ATOMIZED FUELS	
Water Content, % (v/v)	Viscosity (cp) at 100° F.
14	1002.1
16	417.6
23	89.3
27	53.7
33	71.6

Additionally, Amelia Fuel oil was emulsified in various proportions of an aqueous phase consisting of 13.3% (w/w) methanol and 86.7% (w/w) deionized water using a surfactant package ratio of 1:250 based on oil. Viscosities were measured at 100° F. The data are tabulated in Table XXIV.

TABLE XXIV

EFFECT OF AQUEOUS PHASE CONTENT ON VISCOSITY OF AMELIA FUEL OIL PRE-ATOMIZED FUELS	
Aqueous Phase Content, % (v/v)	Viscosity (cp) at 100° F.
18	1074
21	573
24	54
27	38
30	33

In all three cases, as the oil:water ratio was increased, the viscosity similarly increased.

7.3.4. Temperature effects on hydrocarbosols

Hydrocarbosols were prepared at low speed in a blender (as in Section 7.3.1) with Boscan crude oil at oil:water ratios of 72:28 and 63:37 (v/v) using a surfactant package comprising 15% α -emulsan (technical grade), 42.5% Tergitol-NP40 and 42.5% Alfonic 1412-A, (w/w), at a ratio of 1:250 based on oil. The viscosity versus temperature profiles of emulsan-stabilized Boscan crude oil hydrocarbosols were compared to the viscosity versus temperature profiles of the unemulsified crude oil. The temperature effects on hydrocarbosols were much less pronounced than on the crude oil from which the hydrocarbosols were formulated as depicted in FIG. 2.

7.3.5. Comparative static testing

The purpose of these experiments was to determine the stability under static conditions of oil-in-water emulsions of viscous crude oils made with surfactant packages comprising chemical surfactants, with or without bioemulsifier. Specifically, the determination of the

time course over which the oil-in-water emulsions maintained a reduced viscosity without breaking or inverting was desired to assess the ease and success with which such emulsions can be handled for transportation and/or storage purposes. Behavior of viscous crude oil-in-water emulsions was of further interest with regard to the possibility of pump failures and shut-downs during pipelining operations where emulsion stability is desirable to avoid emulsion breakage and circumvent the need to re-emulsify prior to re-start of operations.

Several surfactant packages, the compositions of which are shown in Table XXV, were used to prepare oil-in-water emulsions [oil:water = 70:30 on a volume per volume (v/v) basis] in which the ratio of surfactant package to oil was 1:500 on a weight per weight (w/w) basis. The surfactants used to formulate the surfactant packages of Table XXV are commercially available: Tergitol NP-40 (Union Carbide Corporation) or Alionic 1412-A (Conoco, Inc.). The surfactant packages were formulated with or without α -emulsan (technical grade) as indicated in the table directly below.

TABLE XXV

COMPOSITIONS OF SURFACTANT PACKAGES USED IN STATIC TESTING OF EMULSION STABILITY			
Surfactant Package	% of Component (w/w) in Surfactant Package		
	α -Emulsan	Tergitol NP-40	Alionic 1412-A
A	0	100	0
B	15	85	0
C	0	50	50
D	15	42.5	42.5
E	50	25	25

The method used to prepare oil-in-water emulsions for these experiments was as follows. Into a suitable container, an amount of crude oil was weighed so as to make up 70% (v/v) of the final emulsion. The crude oils used were the Boscan and Texas Fireflood crudes as described in Sections 7.2.1 and 7.2.2, supra and also a Kansas crude. The oil was then heated to 50–60° C. Into a separate container, the particular surfactant package chosen (see Table XXV) was weighed so as to yield a 1:500 ratio (w/w) of surfactant package to oil in the final emulsion. Sufficient make-up water was added to the surfactant package to provide a 30% (v/v) aqueous phase in the final emulsion. Three types of aqueous phases were used: tap water, deionized water, or Texas brine. The Texas brine comprised ions in the following approximate concentrations [in parts per million (ppm)]: sodium, 28,600; calcium, 1,800; magnesium, 290; ferric, 27; barium, 17; chloride, 47,900; bicarbonate, 540; and sulfate, 12. The aqueous phase was added to the oil phase and blended using typical blender blades at low speed, as in Section 7.3.1, i.e., in a manner preventing the beating of air into the emulsion. The individual emulsions were stored in sealed containers for periods of up to 29 days. The viscosity was measured daily with a Brookfield RVT Viscometer (Brookfield Engineering), equipped with an RV3 spindle, at 10 rpm at ambient (70–80° F.) temperature. Five groups of emulsions were subjected to the test and their compositions are indicated in Table XXVI.

TABLE XXVI

EMULSION COMPOSITIONS ¹			
Group	Oil	Aqueous	Surfactant Package ²
1	Texas Fireflood Crude	Tap Water	C D E
2	Boscan Crude	Deionized Water	A B C
3	Boscan Crude	Texas Brine	A B C
4	Texas Fireflood Crude	Deionized Water	A B C
5	Texas Fireflood Crude	Texas Brine	A B C
6	Kansas Crude ³	Tap Water	C D E
7	Kansas Crude	Texas Brine	C D E

¹All emulsions were 70:30, oil:water (v/v).

²Surfactant Packages are defined in Table XXV and were used at 1:500, surfactant package:oil (w/w), except for Groups 6 and 7 where the proportion was 1:1,000.

³Kansas crude oil has a viscosity of 1,127 cp at 76° F. The specific gravity is 0.941 and the API gravity is 18.9° API.

The results for Groups 1–7 (see Table XXVI) are tabulated in Tables XXVII–XXXII, respectively.

TABLE XXVII

STATIC TEST DATA - GROUP 1			
		% α -Emulsan (w/w) in Surfactant Package	
Time (days)	0	15	50
	Viscosity (cp)		
0	155	92	138
1	7850	700	6900
2	8920	720	2802
5	9920	1616	3700
6	10960	1790	6234
7	11385	2425	5130
8	10067	2717	4100
12	9800	2791	3495
13	11820	2107	3900
14	10880	2133	2997
16	10000	2060	2800
19	10200	2060	2570
23	10100	1732	2288
29	11700	1948	2760

TABLE XXVIII

STATIC TEST DATA - GROUP 2			
		% α -Emulsan (w/w) in Surfactant Package	
Time (days)	0	15	
	Viscosity (cp)		
1	65	76	
2	76	84	
3	84	122	
4	91	122	
7	84	129	
9	53	122	
17	60	122	

TABLE XXIX

STATIC TEST DATA - GROUP 3			
		% α -Emulsan (w/w) in Surfactant Package	
Time (days)	0	15	
	Viscosity (cp)		
1	160	152	
2	167	152	
3	144	163	
4	141	129	
7	167	144	

TABLE XXIX-continued

STATIC TEST DATA - GROUP 3		
Time (days)	% α -Emulsan (w/w) in Surfactant Package	
	0	15
Viscosity (cp)		
9	130	129
17	144	122

TABLE XXX

STATIC TEST DATA - GROUP 4		
Time (days)	% α -Emulsan (w/w) in Surfactant Package	
	0	15
Viscosity (cp)		
1	2443	733
2	4492	1775
3	5799	2371
4	5776	2580
7	6616	1847
9	6190	2204
17	5282	2037

TABLE XXXI

STATIC TEST DATA - GROUP 5		
Time (days)	% α -Emulsan (w/w) in Surfactant Package	
	0	15
Viscosity (cp)		
1	114	103
2	137	91
3	106	84
4	110	106
7	110	114
9	99	118
17	84	91

TABLE XXXII

STATIC TEST DATA - GROUP 6		
Time (days)	% α -Emulsan (w/w) in Surfactant Package	
	0	15
Viscosity (cp)		
0	171	114
1	380	342
2	798	633
7	1697	1279
8	1691	1222
11	1526	773
15	1406	602
18	1406	494

TABLE XXXIII

STATIC TEST DATA - GROUP 7		
Time (days)	% α -Emulsan (w/w) in Surfactant Package	
	0	15
Viscosity (cp)		
0	551	418
1	323	228
2	253	171
7	196	133
8	222	133
11	184	114
15	171	114
18	184	114

The results for Group 1 indicate that for emulsions of the Texas fireflood crude in tap water, the addition of 15% (w/w) α -emulsan (technical grade), to a surfactant

package containing co-surfactants Tergitol NP-40 and Alfonic 1412-A was preferable to the addition of 50% (w/w) α -emulsan and was also preferable to excluding α -emulsan from the surfactant package. The results for Group 2 indicate that for emulsions of the Boscan crude in deionized water, the addition of 15% (w/w) α -emulsan to a surfactant package containing Tergitol NP-40 only did not improve viscosity reduction, although the measured viscosities of either emulsion, i.e., with or without α -emulsan, were acceptably reduced. The results for Group 3 indicate that for emulsions of the Boscan crude in Texas brine, the addition of α -emulsan to a surfactant package containing Tergitol NP-40 alone did not yield significantly different results from the surfactant package without α -emulsan. Nevertheless, either surfactant package, i.e., with or without α -emulsan yielded acceptably reduced viscosities. The results further demonstrated that brine can be used as aqueous phase. The results for Group 4 indicate that for emulsions of the Texas fireflood crude in deionized water, the addition of 15% (w/w) α -emulsan to a surfactant package containing Tergitol NP-40 only is preferable to omitting α -emulsan from the surfactant package. The results of Group 5 indicate that for emulsions of the Texas fireflood crude in Texas brine, the addition of α -emulsan to a surfactant package containing Tergitol NP-40 alone did not yield significantly different results from the surfactant package without α -emulsan. Nevertheless, either surfactant package, i.e., with or without α -emulsan yielded acceptably reduced viscosities. Comparison of the Group 4 data with that of Group 5 dramatically illustrates the effect of different aqueous phases on the viscosities of Texas fireflood crude oil-in-water emulsions. The data indicate that the use of Texas brine is preferable to the use of deionized water for forming oil-in-water emulsions with Texas fireflood crude. The results for Groups 6 and 7 indicate that for emulsions of the Kansas crude in tap water or Texas brine, the addition of 15% (w/w) α -emulsan to a surfactant package containing co-surfactants Tergitol NP-40 and Alfonic 1412-A was preferable to the exclusion of α -emulsan from the surfactant package. The data from these groups illustrate how the viscosity versus time profiles of emulsions of the same crude oil can vary dramatically as a function of the aqueous phase and also that the viscosity versus time behavior of one type of crude oil/water emulsion can be significantly different than that of other crude oil/water emulsions.

That the presence of α -emulsan in surfactant packages used to emulsify Texas fireflood crude oil or Kansas crude oil has a significant effect on emulsion stability and maintenance of reduced viscosities can be seen in FIGS. 3, 4, 5 and 6 where the data from Groups 1, 4, 6 and 7 (Tables XXVII, XXX, XXXII and XXXIII for 0% and 15% α -emulsan) are presented graphically. The lower curves in each figure represent the viscosity versus time profiles for α -emulsan-stabilized hydrocarbons. The viscosities of the α -emulsan-stabilized hydrocarbons remain significantly more reduced than that of the emulsions formed with surfactant packages that did not include α -emulsan.

7.3.6. Stabilizer comparisons

An experiment was performed to compare the emulsion-stabilizing effect of α -emulsan with that of known chemical emulsion-stabilizers, naphthalene sulfonate and lignin sulfonate. Specifically, the viscosity versus time profiles at 75° F. were followed for four emulsions containing either α -emulsan, naphthalene sulfonate or lignin sulfonate or no stabilizer at all. All emulsions were formulated with the Texas fireflood crude described in Section 7.2.2. at an oil:water ratio of 70:30 (v/v). Surfactant packages were used at a ratio of 1:500 (w/w) based on oil. The results are shown in FIG. 7. The α -emulsan-stabilized hydrocarbonsol was formulated with a surfactant package comprising 15% α -emulsan (technical grade), 42.5% Tergitol NP-40, and 42.5% Alfinic 1412-A (w/w); its viscosity versus time profile is the curve depicted by closed circles. The naphthalene sulfonate-stabilized emulsion was formulated with a surfactant package comprising 15% naphthalene sulfonate, 42.5% Tergitol NP-40 and 42.5% Alfinic 1412-A (w/w); its viscosity versus time profile is the curve depicted by closed triangles. The lignin sulfonate-stabilized emulsion was formulated with a surfactant package comprising 15% lignin sulfonate; 42.5% Tergitol NP-40 and 42.5% Alfinic 1412-A (w/w); its viscosity versus time profile is the curve depicted by closed inverted closed triangles. A fourth emulsion (the control) was formulated with a surfactant package comprising 50% Tergitol NP-40 and 42.5% Alfinic 1412-A (w/w) with no additional emulsion stabilizer; its viscosity versus time profile is the curve depicted by open squares.

Immediately after emulsion formation a zero time point measurement was taken. Thereafter the emulsions were allowed to remain stationary for 28 days during which time period viscosities of the four emulsions were measured daily to determine the increase, if any, in viscosity. The points in FIG. 7 represented by stars indicate that by day 8 for the naphthalene sulfonate stabilized emulsion and by day 12 for the lignin sulfonate-stabilized emulsion, these two emulsions had failed, i.e., inverted into water-in-oil emulsions. It can be seen from FIG. 7 that under the conditions of the experiment, α -emulsan was a significantly more effective stabilizer of Texas fireflood crude oil:water emulsions than were either of the two chemical stabilizers (lignin sulfonate and naphthalene sulfonate) or the co-surfactants (Tergitol NP-40 and Alfinic 1412-A) alone.

α -Emulsan preparations in the form of purified grade, technical grade, whole broth, supernatant, and *Acinetobacter calcoaceticus* ATCC 31012 bacterial cells (see Section 7.1.) were compared in terms of their ability to form and stabilize emulsions of Oklahoma vacuum resid. All of the emulsions were produced at an oil to water ratio of 70:30 (w/w). The aqueous phase contained 1 part surfactant package to 200 parts oil (w/w). The surfactants present at 85% (w/w) were either Triton-165, Alipal EP-110 or Alipal CO-436. Performance was characterized according to emulsion viscosity, phase separation and degree of hydrocarbon incorporation. Most differences were apparent at 2 or more days following emulsion formation. In all cases the α -emul-

san preparation comprised 15% (w/w) of the total surfactant package present. Technical grade α -emulsan produced less viscous emulsions than the purified product, regardless of the co-surfactants present. The α -emulsan in whole broth, supernatant and cells respond differently depending upon the co-surfactant used. The most advantageous results are seen with the whole broth. Whole broth repeatedly produced more fluid emulsions than the technical and purified products. All α -emulsan preparations were not equally effective in maintaining stable, low viscosity emulsions for extended periods of time. The α -emulsan present in cells has shown variable results in maintaining emulsions exhibiting reduced viscosities, but this material consistently prevented creaming. Additionally, enzyme treatment offers little benefit in the performance of the emulsans for preparing emulsions with this hydrocarbon. Thus, due to the consistent results obtained with whole broth, it is the α -emulsan source of choice for the emulsification of Oklahoma vacuum resid.

α -Emulsans produced by *Acinetobacter calcoaceticus* ATCC 31012 cultures which utilized soap stock as the carbon source displayed results similar to those obtained from cultures grown on ethanol.

Preparations of materials produced by NS strains of *Acinetobacter calcoaceticus* as described in Section 7.1.2. were used to form and stabilize emulsions of Oklahoma vacuum resid. All of the emulsions were produced at an oil-to-water ratio of 70:30 (w/w). The aqueous phase contained 1 part surfactant package to 200 parts oil (w/w). The surfactant present at 85% (w/w) was Alipal CO-436. In all cases the NS materials comprised 15% (w/w) of the total surfactant package.

In addition to the bioemulsifiers, there are conventional synthetic surfactants which are also known emulsion stabilizers: lignin sulfonates and naphthalene sulfonates are examples of such materials. Replacement of α -emulsan with these surfactants also allows production of oil-in-water emulsions. However, the lignin sulfonates do not produce emulsions of reduced viscosity, whereas the naphthalene sulfonates are generally satisfactory replacements for α -emulsan for use with viscous residuals. These naphthalene sulfonates not only produce very fluid emulsions, they also minimize, if not entirely prevent, creaming of the oil. These particular anionic surfactants perform well with all of the co-surfactants mentioned earlier, and will successfully produce emulsions.

7.3.7. Mixing of a slurry with a pre-atomized fuel

The composition of a surfactant package that was successfully used both to form a stable pre-atomized fuel from a California vacuum resid and to form a stable slurry from a ROSE resid is listed in Table XVIII, Package 17. The α -emulsan used was prepared from a technical grade of emulsan as described in Section 7.1.1. The surfactants Lignosol BD (Reed Ltd. Chemical Div.), Triton X series (Rohm & Haas Co.), and Tergitol NP series (Union Carbide Corp.) are commercially available. Both the pre-atomized fuels and slurries were formed in an Osterizer Galaxy 14 blender at high speed in a manner which prevents the incorporation of air into

the resulting dispersion. The ratio of California resid and ROSE resid to their respective aqueous phases was 70:30 by weight (w/w). The surfactant package was used at a ratio of 1:100 (surfactant/hydrocarbon) by weight (w/w) for both the preatomized fuel and the slurry. The surfactant package comprising 42.8% Triton X-405, 28.6% Tergitol NP-40, 14.2% Lignosol BD, and 14.2% technical grade α -emulsan was the preferred surfactant package for use with both California vacuum resid and ROSE resid. Results of mixing the slurry with the pre-atomized fuel are listed in Table XXXIV.

TABLE XXXIV

VISCOSITY OF PRE-ATOMIZED FUEL/SLURRY MIXTURE	
	Viscosity (cp)
1. Pre-Atomized Fuel	220
2 Slurry	515
3. 50/50 Pre-Atomized Fuel/ Slurry by weight (w/w)	175

7.3.8. Formation of pre-atomized fuels at high temperatures under pressure

The composition of a surfactant package that was successfully used to form a stable pre-atomized fuel at a high temperature and under pressure was as follows: 88.5% (w/w) Nacconal 90-F (Stepan Chemical Co.), a linear dodecyl benzene sulfonate and 11.5% α -emulsan whole broth. The α -emulsan used was prepared from a post-fermentation whole broth as described in Section 7.1.2. The ratio of the hydrocarbon phase to the aqueous phase was 70:30 (California vacuum resid/tap water) by weight. The surfactant was used at a ratio of 1:200 (surfactant/hydrocarbon) by weight. The pre-atomized fuel was formed as described in Section 6.3. with the following modification: the pre-atomized fuel was formed at 300° F. and approximately 70 psi pressure was maintained in order to prevent the vaporization of the aqueous phase. The pre-atomized fuel was then cooled to a temperature lower than 212° F. using an appropriate heat exchange device and pressure was released. The foregoing experiment was performed with a surfactant package containing only Nacconal 90-F with similar results.

7.3.9. Formation of pre-atomized fuels using a thermally cracked hydrocarbon discharge

The composition of a surfactant package that was successfully used to form a stable pre-atomized fuel from a German Visbreaker resid was as follows: 50% Triton X-705 (w/w) (Rohm & Haas Co.), 33.3% Tergitol NP-70 (Union Carbide Corp.) and 16.7% whole broth α -emulsan. The α -emulsan used was prepared from a post-fermentation whole broth according to the methods described in Section 7.1.2. The pre-atomized fuel was formed in an Osterizer Galaxy 14 blender at the highest speed setting in a manner which prevents the incorporation of air into the resulting dispersion. The ratio of the hydrocarbon phase to the aqueous phase was 69.2:30.8 by weight (w/w). The surfactant package was used at a ratio of 1:350 (surfactant/hydrocarbon) by weight (w/w).

The method used to form the pre-atomized fuel is described in Section 6.3 with the following modifications: The water used to form the pre-atomized fuel was

divided into two parts: 37.5% by weight of the water was placed in a container and partially frozen to make a slush and 62.5% by weight of the water was combined with the surfactant package and used to form a pre-atomized fuel as described in Section 6.3. The ratio of the hydrocarbon phase to the aqueous phase at this point was 78.3% by weight German visbreaker resid and 21.7% by weight water/surfactant package. The newly formed hot pre-atomized fuel was then combined with the remaining water which had been frozen and the total mixture was immediately placed in an ice bath. This caused an immediate and rapid quenching of the pre-atomized fuel to a temperature at least about 100° F. below the softening point of the hydrocarbon. The pre-atomized fuel produced utilizing this method has been observed to be stable and maintain a reduced viscosity for several weeks.

7.4. Pipelining Pilot test

A pilot scale field test was conducted to determine how a hydrocarbosol would perform under simulated pipelining conditions. Approximately 29 barrels (BBL) of the Boscan crude oil described in Section 7.2.1. were emulsified into approximately 12 barrels of aqueous phase to form an oil-in-water emulsion. The final oil phase to aqueous phase ratio was 70/30 (v/v). The aqueous phase consisted of tapwater supplied by the Tulsa, Oklahoma municipal system (total dissolved solids: 221 ppm; total hardness: 151 ppm). Emulsification was accomplished by mixing warm oil with surfactant-containing aqueous phase using a centrifugal pump. The surfactant package used comprised α -emulsan (technical grade) and Tergitol NP-40 at 15% and 85% by weight, respectively. The surfactant package was used at a treatment rate of 1 part surfactant package to 500 parts oil by weight.

The resulting hydrocarbosol was continuously circulated in a pipe loop at an average velocity of 6.7 ft/sec (3.125 inch I.D., 2,560 feet long) for 96 hours using a centrifugal pump. This is shown schematically in FIG. 8.

During the entire test run the observed hydrocarbosol viscosity remained less than 100 cp. [Pressure drop/flow rate data indicated an apparent viscosity of approximately 70 cp at 60° F. for the hydrocarbosol throughout the operation.] This is in dramatic contrast to the viscosity of the Boscan crude before emulsification, approximately 192,000 cp. At the end of the continuous test period, flow through the loop was interrupted for 64 hours to simulate a pump failure. After three days of shutdown, pumping was resumed with no apparent change in hydrocarbosol characteristics. Pressure drops and flow rates were similar after restart as prior to shutdown. There was no need to reemulsify.

During this test, the hydrocarbosol was pumped an actual physical distance of approximately 380 miles. It traversed the pump once every 17 minutes. In this manner, the hydrocarbosol was subjected to stress (shear) roughly equivalent to being pumped a distance of 26,000 miles in a commercial pipeline (considering pipe diameters, pump transits, flow rates, etc.). Such stress is

known to cause failure (inversion) of oil-in-water emulsions stabilized by conventional surfactants. Laboratory evaluation of the hydrocarbonsol upon completion of the test demonstrated that, should demulsification be desirable, the emulsion could be demulsified readily using standard oilfield techniques. Table XXXV summarizes the pertinent numbers, results, and conditions of the pipelining pilot test.

TABLE XXXV

SUMMARY OF PIPELINING PILOT TEST DATA	
Oil/Water Ratio	70/30
Surfactant Package/Oil Ratio	1/500
Total Running Time	96 hours
Shutdown time prior to successful restart	64 hours
Average flow rate during run	160 gpm
Average flow velocity	6.69 ft/sec.
Pipe I.D.	3.125 inches
Distance pumped	approx. 380 miles
Number of pump transits	approx. 330
Apparent viscosity of emulsion	70 cp
Viscosity of Boscan at 60° F.	190,000 cp
Comparable flow rate in 20" line	210,000 BBL/day
Comparable flow rate in 30" line	475,000 BBL/day

7.5. Direct Combustion Test on Pre-Atomized Fuels

7.5.1. Furnace assembly and instrumentation

The direct combustion test was run in a large scale (1 Megawatt) furnace assembly, essentially comprising in sequential arrangement: a burner, a brick-lined experimental chamber (also called the refractory-lined combustion tunnel), an after burner, a water-cooled (cold-wall) chamber and an exhaust section, approximately 1.14 meters (m), 4.55 m, 1.24 m, 4.55 m and 1.65 m in length, respectively. The other major components of the facility used include the systems for storage, metering, feeding and control of fuels, for pumping, preheating, and metering of the combustion air, and for cleaning and pumping the combustion products.

The furnace assembly is equipped with water-cooled probes for sampling combustion gases which are drawn off under vacuum and pass through a sample transport line to a set of continuous on-line gas analyzers, specifically a Chemiluminescent NO-NOX Gas Analyzer (Thermo Electron Corporation, Model 10A), an Infrared CO Analyzer (Beckman, Inc., Model 865), an Infrared CO₂ Analyzer (Beckman, Inc., Model 865) and a Paramagnetic O₂ Analyzer (Beckman, Inc., Model 755). The furnace assembly is also equipped with a water-cooled suction pyrometer for measuring axial flame temperatures at various flame positions within the experimental combustion tunnel. The furnace assembly is further equipped with water-cooled water quench sampling probes through which combustion gases, including particulates, are drawn off under vacuum, are quenched with water and flow through a sampling train, the first component of which is a filter (paper) for collection of solids. This equipment provides for the quantitation of solids in the combustion gases.

7.5.2. Preparation of pre-atomized fuel for combustion test

The characteristics of the Number 6 residual test fuel oil used as the oil phase of the pre-atomized fuel are described in Section 7.2.3. Table XXXVI summarizes

the ultimate analysis of the fuel oil. Its heating value was 18,384 Btu/lb.

TABLE XXXVI

NUMBER 6 RESIDUAL TEST FUEL OIL ULTIMATE ANALYSIS	
Constituent	%
Carbon	85.63
Hydrogen	10.69
Nitrogen	0.47
Sulfur	2.30
Oxygen	0.91
Ash	0.08
Water	0.10
Asphaltenes	10.44

The Number 6 fuel oil was emulsified in water using a surfactant package comprising 15% α -emulsan (technical grade), 42.5% Tergitol NP-40, 42.5% Alfonic 1412-A (in weight percent). The surfactant package was used at a rate of 1 part per 250 parts oil (w/w). The ratio of oil to water in the resulting pre-atomized fuel was approximately 70:30 (v/v). One hundred ten gallons of pre-atomized fuel were prepared in a fuel preparation system which incorporates a Gaulin mechanical homogenizer. The aqueous solution containing the surfactant package was fed via a centrifugal pump into a mixing-T located in the Number 6 fuel oil supply line. This arrangement provided in-line pre-mixing of the oil and water prior to entering a 45 g.p.h. high-pressure mechanical homogenizer (Gauldin). The minimum homogenization pressure of 1000 psi was employed for producing the preatomized fuel. The resulting pre-atomized fuel had a viscosity ranging from 70-120 cp at 80° F.

Accurate control of both oil and water flow rates are required to maintain a constant 70/30 oil/water mass ratio during this continuous mixing process. Precise control of the water flow proved to be a problem due to the very low flow rates required, and it is estimated that the oil/water ratio varied between 65/35 and 75/25 during production. Two barrels of pre-atomized fuel were produced with the following composition: Barrel #1—71.25% : 28.75% water by weight; and Barrel #2—69.78% oil : 30.22% water by weight. Both barrels of pre-atomized fuel were produced one week prior to the combustion test and no separation was apparent during this time. Prior to the combustion test both barrels were stirred with a slow speed stirrer.

7.5.3. Combustion test procedure

Standard procedures for firing a Number 6 fuel oil in the type of furnace assembly employed were followed with the exception that the in-line fuel heaters were not used, and the pre-atomized fuel was fired at a temperature of approximately 90° F.

The refractory-lined combustion tunnel was brought up to operating temperature (approximately 1000° C.) using natural gas. The gas gun was then removed and replaced by a standard oil gun fitted with a twin fluid atomizer of the Y-jet type. Compressed air at approximately 60 psi was used for the atomizing fluid.

The initial light-off on the oil burner was accomplished using a Number 2 oil as is standard practice. The air and fuel flow rates were then adjusted to give a thermal input of approximately 1 MW or 3.4 MM

Btu/hr. A simple on-load fuel transfer from Number 2 fuel oil to the 70/30 pre-atomized fuel was then effected by transferring the suction hose from the barrel of Number 2 fuel to the barrel of pre-atomized fuel.

A significant reduction in fuel flow rate occurred shortly after transfer to the pre-atomized fuel due primarily to the higher viscosity of the pre-atomized fuel and the resultant pressure drop in the fuel lines. Stable flame conditions were maintained during the fuel transfer but good flame conditions could not be achieved as the fuel flow rate fell below the minimum required.

Initially the drop in fuel flow rate was thought to be due to blockage of the atomizer. The Y-jet atomizer was removed, cleaned, and replaced. Light-off was accomplished without any problem using the pre-atomized fuel but low fuel flow rates prevailed. A second atomizer, of the internal-mix type was then employed. Again light-off using the preatomized fuel presented no problem but the low fuel flow rate persisted.

Finally it was concluded that the flow problem was due to a partially blocked flow control valve. The nature of this blockage was not determined. A manual by-pass valve around the control valve was opened and the pre-atomized fuel-flow rate was increased to a maximum of approximately 4 lb/min (approximately 0.9 MW input). This resulted in an entirely satisfactory flame having visible characteristics very similar to those of a Number 6 fuel oil flame obtained under similar firing conditions.

A stable flame was maintained throughout the remainder of the test period, during which time minimum excess air levels, solids emissions, and axial flame temperatures were measured.

7.5.4. Results of preliminary combustion test

The ignitability and stability of the 70/30 preatomized fuel were found to be comparable with those of a Number 6 fuel-oil when fired under similar conditions in the furnace assembly used.

Flame stability was found to be acceptable even when the important combustion parameters of excess air, minimum fuel flow rate, and atomization conditions were not matched. This occurred inadvertently during light-off and when fuel-flow rates fell below the limits for acceptable flame conditions. However, these results indicated that ignition and flame stability were not major problems of the pre-atomized fuel.

Minimum excess air levels of less than 2% were achieved without any visible smoke or carbon monoxide in the flue gas. These figures compare favorably with those attainable with a Number 6 fuel oil. Table XXXVII summarizes the range of operating conditions examined during this short test in terms of excess air levels and flue gas composition, the major point of interest being the low excess air levels that were obtained.

TABLE XXXVII

EXCESS AIR DATA		
% Oxygen in Flue Gas	% Excess Air	Carbon Monoxide (ppm)
0.61	2.83	0
0.54	2.50	0
0.48	2.21	0
0.44	2.03	0
0.20	0.91	100-150

TABLE XXXVII-continued

EXCESS AIR DATA		
% Oxygen in Flue Gas	% Excess Air	Carbon Monoxide (ppm)
0.16	0.73	150

Pre-Atomized Fuel Input approx. 4 lb/min (0.93 MW Thermal Input)
Pre-Atomized Fuel Temperature 90° F.
Atomizer Air Preheat 500° F.

The visible flame length under these conditions was approximately 6 ft. and the general appearance of the flame was very similar to that of a Number 6 fuel oil flame. The exhaust gas on exit from the high temperature combustion zone appeared to contain a small amount of 'white-smoke', very similar in appearance to that observed when firing coal-water slurries under similar conditions. This 'white-smoke' was not visible on exit from the stack and its nature was not determined.

A water-cooled probe was used to obtain solids samples from the exhaust gas and along the axis of the flame. FIG. 9 shows the concentration profiles along the flame axis for a Number 6 fuel oil and the 70/30 pre-atomized fuel. The solids concentration at the exit from the combustor was almost identical for these two fuels. The solids concentration within the flame was slightly lower for the 70/30 pre-atomized fuel. These two flames were obtained using two different atomizers; nevertheless the data indicate that the carbon burnout achieved with the pre-atomized fuel fired at 90° F. was comparable to that for the parent Number 6 fuel fired at 240° F. to facilitate atomization.

Axial flame temperatures were also measured using a water cooled suction pyrometer and these are shown in FIG. 10. The 70/30 pre-atomized fuel flame exhibited a slightly lower temperature along the entire length of the combustion chamber. This was entirely compatible with the quenching effect expected from the 30% water content. The measured reduction in flame temperature of 100-150° C. does not represent a serious problem in most industrial combustion systems.

7.5.5. Results of combustion emissions test

Subsequent to the above combustion test, another series of test burns were made using the oils and preatomized fuels of these oils, as listed in Table XXXVIII.

TABLE XXXVIII

TEST FUEL SPECIFICATIONS AND EMULSION PROPERTIES

	Edgerton Bunker C	Crude Oil*	Mohawk Bunker C
Specific Gravity	0.99	0.99	0.99
Paraffin	27%	34%	53%
Aromatic	52%	44%	35%
Temp. v. Viscosity			
F	CPS	CPS	CPS
200	59.65	65.60	47.72
180	83.51	87.50	59.65
160	116.91	168.35	71.58
140	214.74	322.10	107.37
120	429.48		190.88

Pre-Atomized Fuel Viscosities 70-150 cp
Pre-Atomized Fuel Specific Gravity = 0.99
*California Kern County

Procedures followed to form the pre-atomized fuels are described, supra. The primary purpose of these burns was to demonstrate the potential emissions reduc-

tions with pre-atomized fuels. In Table XXXIX the results of these burn tests are presented. The results indicate that burning such pre-atomized fuels caused significant reductions in NOX and SO₂ emissions.

TABLE XXXIX

RESULTS OF BURN TESTS WITH PRE-ATOMIZED FUELS			
	Edgington Bunker C	Mohawk Bunker C	Crude Oil*
Baseline NOX (ppm)	550	450	355
Pre-Atomized Fuel NOX (ppm)	270	325	300
% Reduction	51	28	15
Baseline SO ₂ (ppm)	1100	840	300
Pre-Atomized Fuel SO ₂ (ppm)	650	500	250
% Reduction	43	40	17

Pre-Atomized Fuel Viscosities 70-150 cp

Pre-Atomized Fuel Specific Gravity = 0.99

*California Kern County

All Readings made at 1% O₂

It is apparent that many modifications and variations of this invention as hereinabove set forth may be made without departing from the spirit and scope thereof. The specific embodiments described are given by way of example only and the invention is limited only by the terms of the appended claims.

We claim:

1. An improved method for post recovery transporting viscous hydrocarbons, wherein the improvement comprises (A) forming a hydrocarbosal of said viscous hydrocarbons using a surfactant package in a proportion from about 1:500 to about 1:20,000 by weight based on hydrocarbon, said surfactant package comprising:

(1) at least one water-soluble surfactant selected from the group consisting of anionic surfactants, non-ionic surfactants and mixtures thereof, an effective amount of which surfactant promotes emulsification of a hydrocarbon with API gravity of about 20° API or less, viscosity of about 100 centipoise or greater at 150° F., paraffin content of about 50% by weight or less and aromatic content of about 15% by weight or greater into an aqueous phase to form a hydrocarbon-in-water emulsion, the viscosity of which emulsion is reduced by at least a factor of about 10 compared to the viscosity of the hydrocarbon; and

(2) α-emulsan, an effective amount of which α-emulsan stabilizes a hydrocarbon-in-water emulsion formed with a hydrocarbon as in (1) by maintaining viscosity reduced by at least a factor of about 10 for a period of at least about a day under static conditions, said hydrocarbosal (a) comprising a hydrocarbon with API gravity of about 20° API or less, viscosity of about 100 centipoise or greater at 150° F., paraffin content of about 50% by weight or less and aromatic content of about 15% by weight or greater, and (b) having a hydrocarbon:water ratio from about 65:35 to about 75:25 by volume; and (B) transporting the hydrocarbosal.

2. The method of claim 1 wherein the surfactant package comprises from about 50% to about 99% by weight of a water-soluble nonionic surfactant selected from the group consisting of (i) an ethoxylated alkyl phenol represented by the formula $R_xC_6H_4(OC_2H_4)_nOH$ wherein R represents an alkyl group containing from about 8 to about 12 carbon atoms, x represents the number of alkyl groups ranging from about 1 to about 2,

and wherein n represents the number of ethoxy groups ranging from about 1 to about 100; (ii) an ethoxylated alcohol represented by the formula $R(OC_2H_4)_n$ wherein R represents a branched or linear aliphatic group containing from about 6 to about 18 carbon atoms and wherein n represents the number of ethoxy groups ranging from about 2 to about 100; and (iii) a polyoxyalkylated amine represented by the formula $R_xN_y(CH_2)_z$ wherein R represents an oxyalkyl group containing from 2 to 3 carbon atoms, x represents the number of oxyalkyl groups ranging in number from about 4 to about 500 and y represents the number of nitrogen atoms ranging from about 1 to about 2; and from about 1% to about 50% by weight of α-emulsan.

3. The method of claim 1 wherein the surfactant package comprises from about 90% to about 80% by weight of a water-soluble anionic surfactant selected from the group consisting of (i) a sulfated ethoxylated alkylphenol represented by the formula $RC_6H_4(OC_2H_4)_nOSO_3M$ wherein R represents an aliphatic group containing at least about 8 or 9 carbon atoms, n represents the number of ethoxy groups ranging from about 1 to about 100, and M is ammonium, sodium, potassium, calcium or triethanolamine; (ii) an ethoxylated alcohol sulfate represented by the formula $R(OC_2H_4)_nOSO_3M$ wherein R represents an aliphatic group containing from about 6 to about 16 carbon atoms, n represents the number of ethoxy groups ranging from 0 to about 4, and M is ammonium, sodium, potassium, calcium or triethanolamine; and (iii) an alkylarylsulfonate represented by the formula $R_nAr_m(SO_3)_xM$ wherein Ar is an aromatic group which is benzyl, naphthyl, phenyl, tolyl, xylyl or ethylphenyl, R is a linear or branched chain alkyl group containing about 2 to about 16 carbon atoms, n is 1 or 2, m is 1 or greater, x is at least about 1, and M is ammonium, sodium, calcium, potassium or triethanolamine; and from about 10% to about 20% by weight of α-emulsan.

4. The method of claim 1 wherein the surfactant package comprises from about 50% to about 99% by weight of a combination of (i) a water-soluble nonionic ethoxylated alkyl phenol represented by the formula $R_xC_6H_4(OC_2H_4)_nOH$ wherein R represents an alkyl group containing from about 8 to about 12 carbon atoms, x represents the number of alkyl groups ranging from about 1 to about 2, and wherein n represents the number of ethoxy groups ranging from about 1 to about 100 and (ii) a water-soluble anionic ethoxylated or nonethoxylated alcohol sulfate represented by the formula $R(OC_2H_4)_nOSO_3M$ wherein R represents an aliphatic group containing from about 6 to about 16 carbon atoms, n represents the number of ethoxy groups ranging from about 0 to about 4, and M is ammonium, sodium, potassium, calcium or triethanolamine, said combination being in a proportion of about 1:1 by weight; and from about 1% to about 50% by weight of α-emulsan.

5. The method of claim 1 wherein the surfactant package comprises a combination of about 42.5% by weight of ethoxylated monononylphenol with about 40 ethoxy groups and about 42.5% by weight of an ammo-

nium salt of poly(3)ethoxy C₁₂-C₁₄ linear primary alcohol sulfate; and about 15% by weight of α -emulsan.

6. The method of claim 1 wherein the surfactant package comprises a combination of about 42.5% by weight of ethoxylated monononylphenol with about 40 ethoxy groups and about 42.5% by weight of ethoxylated monooctylphenol with about 40 ethoxy groups; and about 15% by weight of α -emulsan.

7. The method of claim 1 wherein the surfactant package comprises a combination of about 50% by weight of an ethoxylated monooctylphenol with about 70 ethoxy groups and about 33% by weight of an ethoxylated monononylphenol with about 70 ethoxy groups, and about 17% by weight of whole broth α -emulsan.

8. The method of claim 1 wherein the surfactant package comprises a combination of about 43% by weight of an ethoxylated monooctylphenol with about 40 ethoxy groups; about 29% by weight of an ethoxylated monononylphenol with about 40 ethoxy groups; and about 14% by weight of a salt of a lignosulfonate, and about 14% by weight of whole broth α -emulsan.

9. The method of claim 1 wherein the α -emulsan of the surfactant package is produced by *Acinetobacter calcoaceticus*.

10. The method of claim 1 wherein the α -emulsan of the surfactant package is produced by *Acinetobacter calcoaceticus* ATCC 31012.

11. The method of claim 1 wherein the α -emulsan of the surfactant package is produced by *Acinetobacter calcoaceticus* NRRL B-15847.

12. An improved method for post-recovery transporting viscous hydrocarbons, wherein the improvement comprises (a) forming a hydrocarbosal of said viscous hydrocarbons using a surfactant package in a proportion from about 1:500 to about 1:5,000 by weight based on hydrocarbon, said surfactant package comprising about 15% by weight α -emulsan and about 85% by weight ethoxylated monononyl phenol with about 40 ethoxy groups, said hydrocarbosal (i) comprising a hydrocarbon with API gravity of about 20° API or less, viscosity of about 100 centipoise or greater at 150° F., paraffin content of about 50% by weight or less and aromatic content of about 15% by weight or greater, and (ii) having a hydrocarbon:water ratio from about

65:35 to about 75:25 by volume; and (b) transporting the hydrocarbosal.

13. An improved method for post-recovery transporting viscous hydrocarbons, wherein the improvement comprises (a) forming a hydrocarbosal of said viscous hydrocarbons using a surfactant package in a proportion from about 1:500 to 1:5,000 by weight based on hydrocarbon, said surfactant package comprising about 15% by weight α -emulsan and about 85% by weight of ethoxylated monooctyl phenol with about 40 ethoxy groups, said hydrocarbosal (i) comprising a hydrocarbon with API gravity of about 20° or less, viscosity of about 100 centipoise or greater at 150° F., paraffin content of about 50% by weight or less and aromatic content of about 15% by weight or greater and (ii) having a hydrocarbon:water ratio from about 65:35 to about 75:25 by volume; and (b) transporting the hydrocarbosal.

14. The method of claim 12 or 13 wherein the water is fresh water.

15. The method of claim 12 or 13 wherein the water is brine.

16. The method of claim 12 or 13 wherein the hydrocarbosal is transported by ship, barge or tanker.

17. The method of claim 12 or 13 wherein the hydrocarbosal is transported by pumping it through a pipeline.

18. The method of claim 12 or 13 wherein the hydrocarbosal has a hydrocarbon:water ratio of about 70:30.

19. The method of claim 12 or 13 wherein the hydrocarbosal is formed from a hydrocarbon selected from the group consisting of Boscan crude oil, Texas fireflood crude oil, Number 6 residual fuel oil, Jibaro crude oil, El Jobo crude oil, Kansas crude oil, California vacuum residual oil, Oklahoma vacuum residual oil, German visbreaker residual oil, Texas visbreaker residual oil, catalytic hydrogenated residual oil, ROSE residual oil and cutback tar.

20. The method of claim 12 wherein the hydrocarbon is Boscan crude oil and the hydrocarbon:water ratio in the hydrocarbosal is about 70:30.

21. The method of claim 20 wherein the hydrocarbosal is transported by pumping it through a nonheated pipeline.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,821,757
DATED : April 18, 1989
INVENTOR(S) : Michael Hayes et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In Column 52, claim 13, line 8, after "to" and before
"1:5,000" insert -- about --.

In Column 51, claim 12, line 39, "hdyrocarbons" should
read -- hydrocarbons --.

In Column 52, claim 17, line 28, "hdyrocarbosal" should
read -- hydrocarbosal --.

Signed and Sealed this
Fifteenth Day of May, 1990

Attest:

Attesting Officer

HARRY F. MANBECK, JR.

Commissioner of Patents and Trademarks

EP.0043843

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(54) Title: HYDROCARBON WATER FUELS, SLURRIES AND OTHER PARTICULATE MIXTURES (57) Abstract The first aspect of the invention involves stable emulsions of hydrocarbons and water using a combination of a low molecular weight agent and a high molecular weight material. In another aspect of the invention slurries are formed for fuel purposes utilizing coal particles with hydrocarbons and water and the aforesaid agent and material to achieve a stable combination or non-combustible materials with water alone or in conjunction with other liquids using the aforesaid agent and material. The present invention also is useful as transportation agents in pipelines, to lower pumping costs.		

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DESCRIPTIONHYDROCARBON WATER FUELS, SLURRIES AND OTHER PARTICULATE MIXTURES

This application is a continuation-in-part application of our co-pending United States Application Serial No. 771,272, filed on February 23, 1977.

Hydrocarbons and water mixtures have many
5 potential uses, such as in internal combustion engines and as a fuel for heating purposes, either in themselves or combined with coal in a coal slurry, or when combined with combustible or non-combustible solids or even with water or oil as the sole liquid.
10 It is believed that emulsions of hydrocarbons and water have not come into general use because of the relative instability of emulsions involving agents in the fuel in economical quantities. However, the need for stable emulsions of hydrocarbons and water has become
15 more important with the increasing price of fuel.

For many years it has been the practice to inject water into fuel systems for purposes of improving engine performance. It has also been recognized that water injection will enable combustion to occur at a
20 lower temperature, thereby decreasing the formation of oxides of nitrogen, which are major pollutants.

In preparing satisfactory emulsions of hydrocarbons and water, it is necessary that the resulting product have satisfactory properties for use in the
25 internal combustion engine. However, with heating uses, the fuel is normally fed into or atomized in a heating

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chamber. Moreover, it is necessary that any emulsion used as a heating fuel have sufficient stability to retain its properties until the time comes for its use. It has been proposed to add coal to oil including crude
5 oil, but such proposals have thus far proved unsuccessful because of the inability to maintain the coal in a stable suspended state in the oil for the usual passage of time between manufacture and commercial use.

It is accordingly a principal object of the
10 present invention to provide stable emulsions of hydrocarbons and water for general fuel use, either with an internal combustion engine, for heating purposes, for jet engines and turbines or general use. Also, contemplated are slurries, such as coal slurries which can
15 be readily transported.

It has been recognized that hydrocarbon-water emulsions can be formed using surfactants as disclosed in U. S. Patent No. 3,527,581. It has also been proposed to use blends of polyoxyethylene emulsifiers in a paper
20 by Peters and Stebar entitled "Water-Gasoline Fuels-Their Effect on Spark Ignition Engine Emissions and Performance" which was presented at the Society of Automotive Engineers, Inc., St. Louis, Missouri, on June 7-10, 1976. Such emulsions contain substantial amounts of water, but are
25 either not stable over long periods of time or require such high quantities of emulsifiers to achieve satisfactory stability as to be uneconomical.



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Additional teachings of hydrocarbon-water emulsions for various purposes are disclosed in U. S. Patents 3,206,410, 3,311,561, 3,346,494, 3,442,842, 3,355,394, 3,645,903 and 3,876,391.

5 The emulsions of the present invention are preferably water and gasoline, jet fuel, heating oil, diesel oil, crude oil, coal slurries and non-combustibles.

10 In accordance with the principles of the present invention, the suspended droplets and/or particles are relatively large and have a size usually in excess of about 1400 Angstroms. Thus, the emulsions of the present invention are more properly termed microemulsions and have a milky appearance or black
15 when coal is used. This is to be compared with microemulsions wherein the internal phase is present in a much smaller droplet and/or particle size so that a microemulsion has a translucent or transparent appearance.

20 With the present invention the continuous phase is at times the hydrocarbon so that the emulsions are so-called water-in-oil emulsions. Other times the continuous phase is water so the emulsion is oil-in-water.

25 Where the water percentage is less than 30% by weight, it can be regarded as a low internal phase ratio. In the range of 30% to 70% water by weight, it is present



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as a medium internal phase ratio and above 70% as a high internal phase ratio system, when water is the internal phase.

One of the advantages offered by the emulsions of the present invention is the great stability over long periods of time, usually well in excess of two months which satisfies usual storage and transportation requirements. Moreover, the viscosity of certain of the emulsions of the present invention is relatively low (about 1 centipoise), although the sedimentation of an emulsion (and therefore its instability) increases as viscosity is lowered. However, the present invention presents a satisfactory balance of high stability and low viscosity. In other applications of invention, high viscosity as well as high stability are afforded. Also, with the present invention satisfactory vaporization is achieved under conditions of reasonably low viscosity and satisfactory stability.

Another characteristic of the invention is that it is usual to have water present in an amount of about 1 to 20% volume with the upper limit reaching 40% by volume or more.

The emulsions of the present invention are achieved by using the combination of (1) a water or hydrocarbon soluble (ionic or noionic) relatively low molecular weight agent (molecular weight in many instances of the order of 1000) which is generally a substance



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wherein one side or part of the molecular is hydrophillic and the other side is lipophillic and (2) a high molecular weight material (of the order of 500,000 or more) that is swellable in water (cross-linked) and/or is
5 water soluble (substantially non-cross-linked).

The combination of the agent and the high molecular weight material creates an extremely stable bond between the water and the hydrocarbon. At the same time, in many instances, the aforesaid combination achieves a
10 low viscosity even where the water is present in excess of 25% by volume. It will be seen that the present invention also contemplates the use of one or more agents, or one or more high molecular weight materials, or a combination of two of one material and one of the other,
15 or vice or versa, or two or more of each material.

The present invention is believed to function satisfactorily with a wide range of hydrocarbons and particularly various gasolines of high or low octane and other well known fuels. However, the present invention
20 also applies to other hydrocarbons and other carbon containing materials such as coal or even non-hydrocarbons such as carbon or even inorganic materials and combustibles which may be introduced or dispensed in oil as a coal slurry with the dispersed particles being present
25 in a size smaller than 60 mesh and preferably 200 to 325 mesh. When the present invention is used in connection with oils for heating purposes, it is demonstrated that



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many well known heating oils, such as #1, #2 or #6 may be used in a water and oil emulsion with suspended coal and/or carbon particles or other particles, both combustible and non-combustible. Examples of non-combustibles are lime, chalk, alumina and others.

Because the emulsions prepared in accordance with the present invention are extremely stable, such emulsions are usable in the same way as presently available furnace heating oil. Moreover, coal particles can be suspended and held suspended in the emulsion with coal present in as much as 50% by weight and sometimes in an even greater amount. Also, the presence of water in the emulsion may improve combustion performance because of the micro-explosions as discussed hereinafter.

In some instances the coal can be suspended in water through the practice of the present invention with the use of little or no oil at all.

A very important consideration arising from the present invention is that the presence of water in the stable emulsion serves to create micro-explosions of water when the emulsion of the present invention is used in an internal combustion engine or in a heating system. Such micro-explosions arise from the superheating of the water in the emulsion. The effect achieved is the blowing of the oil particles apart throughout the hydrocarbon. It is believed that the aforesaid micro-explosions have the effect of substantially increasing the performance



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of the combustion process.

In heating or use in a diesel engine the oil is normally simply fed into or atomized in a heating chamber or injected therein. Thus, the present invention has use
5 for heating or diesel engine purposes and is especially attractive in the formation of stable coal slurries.

Another contemplated use of the present invention is with a herbicide or a plant growth regulator which will be collectively referred to as an agriculturally
10 active agent. An example of an agriculturally active agent usable with the present invention and water to form a stable emulsion is 2,4D.

One agent used in connection with the present invention is sold by the American Cynamid Company and
15 is identified as product OT-100. This agent is the sodium salt of dioctylsulfosuccinnic acid. A second agent usable in connection with the present invention is the sodium salt of decylbenzenesulfonic acid. A third agent is Toximul MP (sulfonate/non-ionic blend) sold by
20 the Stepan Co. This is calcium dodecyl benzene sulfonate and alkyl phenoxy polyoxyethylene ethanol. A fourth agent is Triton X45, sold by the Rohm & Haas Company, which is octylphenoxy polyethoxy ethanol.

Examples of high molecular weight materials usable
25 in the present invention are Carbopol 941 either in acid form or in the completely neutralized form using sodium hydroxide, sodium carbonate, ammonia and other well known



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neutralizing agents, in stoichiometric amounts or otherwise. Carbopol 941 is a high molecular weight polyacrylic acid as disclosed in U. S. Patent 2,798,053.

A second example of a high molecular weight material
5 is an acrylamide/sodium acrylate identified as Dow XD 8992 as disclosed in U. S. Patent 3,699,103 and is partially crosslinked.

A third example of a high molecular weight material is a hydrolized starch polyacrylonitrile graft
10 copolymer as disclosed in U. S. Patent 3,935,099. A fourth example of a high molecular weight material is a high molecular weight polyoxyethylenecoagulant of Union Carbide Company, where the molecular weight is in excess of five hundred thousand.

15 Yet another advantage of the present invention lies in the fact that relatively small amounts of the agent and high molecular weight materials are used. Indeed an effective amount of the agent can be as low as 3.7 grams per liter of gasoline, down to as low as one
20 gram per liter or slightly less. In some instances it is desirable to combine two of the aforementioned high molecular weight materials such as the Carbopol 941 (in the form of the sodium salt or otherwise) and the Dow XD 8992 in formulating the stable emulsion of the
25 present invention. In any event, the present invention contemplates, irrespective of the particular high molecular weight material and low molecular weight agent

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being employed, that in many cases relatively small quantities of the high molecular weight material and low molecular weight agent may be used to achieve a highly stable mixture. This, of course, constitutes a significant advantage of the invention in terms of achieving a highly stable mixture at a relatively low cost. It has been found that the high molecular weight agent may be present in quantities as low as 100ppm, total weight mixture, but concentrations in the neighborhood of 1000ppm are generally preferred as a minimum. With reference to the low molecular weight agent, a minimum concentration of 500ppm is acceptable in some cases, but the generally preferred minimum is about 1000ppm. Of course, there are some mixtures involving certain components which will require significantly higher amounts of stabilizing materials as can be determined by ordinary experimentation.

The agent is added directly at times to the hydrocarbon with the high molecular weight material in aqueous solution or mixture then added to the hydrocarbon agent solution. In some instances, for example when using Triton X45, it is added to the water, rather than to the hydrocarbon because of the special solubility of Triton X45. This is followed by gentle mixing at room temperature immediately, or for some short period of time, usually not more than fifteen minutes to achieve a white or milky macroemulsion. The emulsions



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acheived through the present invention are so stable as to remain intact under short term centrifuge tests and temperature tests and storage tests for periods of time of sixty days or more as required by industry.

5 When used in a coal slurry, it is possible to use less liquid hydrocarbon or none at all because coal, carbon particles or other particulate heat giving material may be added to enhance the heat value of the emulsion. For example, an emulsion produced in accordance with the invention for heat purposes is composed of 10 50% by weight coal, 40% by weight heating oil and 10% by weight water. Alternatively, another coal slurry produced in accordance with this invention is composed of 50% by weight of water and 50% by weight of coal, 15 although the amount of coal can be even greater. Also, bituminous coal, lignite and solvent refined coal may be used.

 It should be kept in mind that in formulating emulsions in accordance with the present invention that 20 the use of greater amounts of the high molecular weight material generally allows the use of smaller amounts of the agent. This is important where the quantity of the high molecular weight material is less expensive than the quantity of the agent. From the examples in the 25 Specification of this Application, it will be seen that relatively low quantities of both the high molecular weight material and the agent are used so that emulsions



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prepared in accordance with the invention are competitively priced. Thus, where the agent is present in relatively low levels, the high molecular weight material
5 is effective to lower the amount of the agent that is needed. However, at higher levels of agent, it tends to dominate the high molecular weight material to the extent that in some cases the agent alone will produce a satisfactory, albeit extremely expensive emulsion.

10 It has also been observed that emulsions are more rapidly formulated when the high molecular weight material is of the swellable type. Moreover, with the increase of water in the internal phase, that is from low to medium or medium to high, viscosity will increase.
15 Conversely, where the water is in the external phase, an increase of water will lower viscosity.

From the foregoing, it can be seen that the emulsions of the present invention are more stable and are macroemulsions which give rise to micro-explosions
20 when consumed, to achieve better engine and/or burning efficiency. Moreover, with the present invention, coal including bituminous coal, lignite and solvent refined coal and other combustible materials like carbon particles or non-combustible materials can be stabilized for
25 a long period of time for transportation or storage.

Where desired, the viscosity and volatility can be adjusted using suitable materials or solvents, such



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as alcohols, like methyls, ethyl or isopropyl alcohol, ketones such as acetone, ethers, etc.

It is theorized that the high molecular weight material provides a generic matrix structure or has the effect of structuring the overall mixture in order to hold very tightly the various components. While Applicants do not wish to be bound by any particular theory, it is believed that the high molecular material of the present invention provides a matrix wherein the water is usually latched onto the matrix with the agent acting as a hook between the water phase and the hydrocarbon phase. Stated more broadly, the theory is that the present invention provides a matrix wherein the water has an affinity for the matrix with the agent having an affinity between the water phase and the hydrocarbon phase.

While in many instances the water is structured or functions as a matrix, the hydrocarbon can also be structured, for instance through the use of aluminum salts of naphthenic acids and coconut oil acids or a mixture of naphthenic acid and unsaturated acids with the agent and water. In many instances the agent is a surface active agent, although the invention is not limited to such a feature.

It is also contemplated that the agent be present in either the water or hydrocarbon phase or both.

It is also contemplated that other additives may be included, such as sodium chloride and other salts,



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the presence of which prevents the formation of a high internal phase ratio material.

Certain examples of the invention will now be provided for the sake of illustration and not by way
5 of limitation. In these examples certain abbreviations have been used.

The low molecular weight agent will have the following abbreviations:

S1 American Cyanamid Company- OT-100- sodium
10 salt of dioctylsulfosuccinnic acid.

S2 Arco Chemical Company- Altrawet DS - sodium
salt of decylbenzenesulfonic acid.

S3 Stepan Company- Toximul MP - calcium dodecyl
benzene sulfonate and alkyl phenoxy polyoxyethylene
15 ethanol.

S4 Rohm & Haas Company - Triton X45 - octylph-
enoxypolyethoxy ethanol.

S5 Imperial Chemical Company, Inc. (ICC U.S.)
Arlacel C Sorbitan sesquioleate.

20 S6 Imperial Chemical Company, Inc. - Tween 40
polysorbate 40 (polyoxyethylene 20 Sorbitan mono palm-
itate).

S7 Proctor & Gamble (Ivory liquid detergent)
U. S. Patents 3,024,273, 3,179,598, 3,179,599 and
25 3,793,233.

S8 Stepan Chemical - Ninate 401 - Calcium
dodecyl benzene sulfonate.



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S9 Stepan Chemical - (Ninate 411) - alkylamine
dodecyl benzene sulfonate (burns completely-contains no
metal).

- 5 S10 BASF Wyandotte Co. - (ES 7071 AS)
S11 BASF Wyandotte Co. - (ES 7071)
S12 BASF Wyandotte Co. - Plurodot - (HA 430)
S13 BASF Wyandotte Co. - Plurodot - (HA 450)
S14 BASF Wyandotte Co. - (ESO 14734)
S15 BASF Wyandotte Co. - Pluropac - (D-25)
10 S16 BASF Wyandotte Co. - Pluropac - (T-55)
S17 BASF Wyandotte Co. - (E8 7312)
S18 ICI (Imperial Chemical Industries) - IL-540
(settled) and (mixed)
S19 Diamond Shamrock Co. - (Fuelspere 55)
15 S20 Diamond Shamrock Co. - (Modicel VD)
S21 General Electric Co. - (SF 1066 Silicone)
S22 Diamond Shamrock Co. - (Fuelsperse 70)
S23 Diamond Shamrock Co. - (Fuelsperse 042)
S24 Monsanto Chemical Co. - (MTS 2049)
20 S25 Monsanto Chemical Co. - (MTS 2050)
S26 Monsanto Chemical Co. - (MTS 2052)
S27 Monsanto Chemical Co. - (MTS 2053)
S28 Monsanto Chemical Co. - (MTS 2054)
S29 Stepan Co. - (Makon 14)
25 S30 Stepan Co. - (Makon 4)
S31 Stepan Co. - (Makon 30)
S32 Stepan Co. - (Makon 8)



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S33 ICI (Imperial Chemical Company - (IL 540)
(new)

S34 Monsanto - (MTS 2056)

S35 Monsanto - (MTS 2057)

S36 Stepan Chemical Co. - (Stepantan-A)

5 The high molecular weight material will have the following abbreviations:

Q1 Dow Chemical Company XD 8992 (1300 swell-
able poly (acrylamide/sodium acrylate) partially cross-
linked as discussed in U. S. Patent No. 3,699,103.

10 Q2 General Mills Company SG-P 502S swellable
hydrolyzed starch polyarylonitrile graft copolymer as
disclosed in U. S. Patent No. 3,935,099.

Q3 B F Goodrich- Carbopol 941 - water soluble
high molecular weight polyarylic acid as disclosed in
15 U. S. Patent No. 2,798,053 in the completely neutralized
form using sodium hydroxide, sodium carbonate or ammonia
or other bases in stockiometric amounts or otherwise.

Q4 Union Carbide Company - Polyoxy Coagulant
(MWM more than 500,000) polyoxyethylene

20 Q5 Dow Chemical Company - Separan MG 700
partially hydrolized polyacrylamides as discussed in
U. S. Patent No. 3,825,069.

Q10 Irradiated carbose (gamma carbose) - This
was prepared by starting with Carbose (sodium
25 carboxymethylcellulose). Manufactured by BASF Wyandotte
Co. The Carbose IM was exposed to gamma radiation and the
Carbose (which is a polymer becomes cross-linked. The gamma



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radiation was obtained by using a batatron-20 MEV (million electron volts) gamma rays for 1 hour. This compound will be referred to hereinafter as irradiated polymerized sodium carboxymethylcellulose.

- 5 Q14 Polybutadiene - (oleophilic)
 Q15 Polyvinyl acetate - (oleophilic)
 Q16 Polystyrene - (oleophilic)
 Q18 Stasorb 372 - A. E. Staleg Co. (similar to
 Q2). See page 23 of Chemical & Engineering News, Nov.
10 5, 1979.

Also usable in the present invention are transportation compositions which facilitate movements of the various emulsions, slurries, etc. through piping, pumps and pumping requirements by lowering pipe friction. The transportation agent is used in a pre-treatment step prior to
15 pumping. One example is the use of Q4 as a pre-treatment in the pipe or as incorporated in the mixture. Also usable in the present invention are transportation materials and agents selected from one or more of the S's and Q's specified above but not limited thereto.
20

The concept of "transportation" referred to hereinabove is particularly directed to the transportation of oil or coal oil mixtures or coal, oil and water mixtures through pipe lines over long distances. As a general
25 aspect, the invention is quite useful as a lubricant for container surfaces and conduits in general. The use of certain aspects of the present invention, as will now be described, substantially lowers the pipe



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friction in order to greatly reduce pumping requirements.

It has been found that S* materials alone are fairly good transportation adding (hereinafter referred to as transportation) materials. The S material can be incorporated into the body of the fluid solution or mixture being transported or can be applied in a precoat-
5 ing step to the inside wall of the pipe. It is preferred that the S material in water solution or in an emulsion or other transportation agent be applied by direct in-
10 jection into the pipe or other conduit container at various pumping stations along the length of the pipe. As such, the transportation agent generally has a lubricating function, and can be regarded as a lubricant.

It has been further found that a combination of
15 Q's and S's will act as a transportation agent as well as a stabilizing agent. For instance, an emulsion**of gasoline and water or kerosene and water can be prepared using various combinations of Q's and S's in accordance with the present invention. This technique involves
20 injecting the aforesaid emulsion of the Q and S material as a lubricant into the pipeline at pumping stations along the pipeline. Where the S material is used alone, a solution of the S material in water.

*Such as S4

**having an S and Q material at a combined concentration of at least 1000ppm of total emulsion weight.



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It has been further found as a part of the present invention that silicates, such as sodium or potassium silicate are quite useful, either alone or in combination with certain S materials as transportation agents. One aspect of this feature of the invention involves blowing a water solution of silicates through the pipe in a precoating stage. Another aspect of the invention involves preparing a water solution or emulsion involving a silicate and a Q and a S and then blowing the entire mixture through the pipeline or injecting the same into the pipeline at pumping stations along the pipeline. In making up a solution of silicate, Q and S, it has been found that the silicate should be present in an amount of at least 1000ppm concentration based on the total weight of the solution or emulsion. A preferred material is S9 when used with silicates only. For coal and oil mixtures or coal, oil and water mixtures, the use of Q4 by itself has a transportation agent has also quite satisfactory.

The preferred silicate is sodium silicate wherein there may be two, three or four molecules of silicon dioxide to one molecule of disodium oxide.

In the following Examples the gasolines are:

- (A) American Oil Co. (AMOCO) Premium (No lead)
av. octane # = 95.7 H₂O means distilled water.
- (B) Same as above, but sub-regular (No lead)



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average octane # = 88.0.

EXAMPLE 1

75 parts by volume of Gasoline A containing
3.75 g/lit. of OT-100 of American Cyanamide were shaken
5 with 25 parts by volume of water, containing 0.7 g/lit.
of Dow Chemical Company's DX-1300 and 0.5 g/lit. of
Na-941 carboplate of B F Goodrich Chemical Co. A
stable emulsion of gasoline/water was produced; on
standing for one month at room temperature no noticeable
10 separation took place; however, after 4.0 months a water
layer, equalling 3.7 volume % of the total liquid appeared;
after 9.0 months the separation of the aqueous layer was
5.6 volume % of the total liquid. The foregoing mixture
was used as a fuel in a single cylinder internal combust-
15 ion engine. Before use, viscosity was lowered by the
addition of ethyl alcohol (10% by volume). The engine
operated satisfactorily under full load for an extended
period of time.

EXAMPLE 2

20 90 parts by volume of gasoline B containing 3.75
g of OT-100 of American Cyanamide Co./lit. gasoline were
shaken with 10 parts by volume of water containing 1.0
g/lit. of a water swellable polymer SGP-5025 of General
Mills Chemicals, Inc. producing a stable milk-like
25 emulsion of gasoline/water. There was no separation of
an aqueous layer after 30 days and after 100 days an
aqueous lower layer approximately 0.5% of the total



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liquid accumulated.

EXAMPLE 3

75 parts by volume of gasoline A containing 3.75 g/lit of gasoline of OT-100 were mixed and shaken with
5 25 parts by volume of water containing only 1.0 g/lit. solution of Na/941/carbopolate. It formed a stable milk-like emulsion so that in 2 weeks no aqueous layer separated and after 100 days 3.3 volume percent of the total liquid separated.

10 EXAMPLE 4

Similar to Examples 1, 2 and 3 emulsions were prepared with the same agents and materials but using instead of gasoline:

- 15 a) Fuel Oil No. 1
b) Fuel Oil No. 2
c) Jet Engine Fuel J P 4
d) Angolan Crude Oil as is.

All of these four types formed stable emulsions, similarly to those of examples 1, 2 and 3.

EXAMPLE 5

20 50.0 parts by weight of No. 2 fuel oil, containing 3.75 g/lit of OT-100 of American Cyanamide were mixed with 30.0 parts by weight of bituminous coal passing a 325 mesh sieve, into a black asphalt-like liquid, after
25 adding 1.65 parts by weight of isopropyl alcohol to wet part of the coal powder. 20.0 parts by weight of water containing both 1 g/lit. of sodium 941-carbopolate of B F Goodrich Chemical Co. and 1 g/lit, XD-8992 of Dow

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Chemical Co. were mixed in by stirring and a 30% weight of coal. (20% weight water) 50% fuel oil slurry produced). It exuded only 3 weight percent of fuel No. 2 after standing for 45 days at room temperature ($\pm 20^{\circ}\text{C}$) and
5 after a temperature cycle of 27 hours at -12°C) and after a temperature cycle of 27 hours 27 hours at -12°C and 4 hours at 85°C to 100°C to 85°C .

EXAMPLE 6

46 parts by weight of the same mesh coal as in
10 Example 5 were mixed with $44\frac{1}{2}$ parts by weight Crude from Angola (light crude) containing 3.75 g/lt. crude of American Cyanamide's OT-100. To this black liquid 10 parts by vol. of water containing the same ingredients and concentrations as in Example 5 above, were added and
15 stirred with a stirrer to a homogenous black slurry of the composition:
46 w/o (weight percent) carbon $9\frac{1}{2}$ w/o water -- $44\frac{1}{2}$ w/o Gulf crude and which persists for long periods of time.

20 EXAMPLE 7

Speed up of inversion

a) To 20cc of H_2O was added 80cc Gasoline B containing S1 (3.75 g/l Gasoline B) and mixed with gentle stirring in a magnet stirrer. The stirring sequence was 15
25 seconds stirring plus 5 seconds standing or manual swirling. After six such sequences the two separated layers rapidly formed a high internal phase ratio emulsion (gas in water) or an invert.



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b). Repeat (of a) except that 18cc of water solution containing Q1 (0.63 g/l H₂O) was added to 73cc of Gasoline B with S1 (3.75 g/l gasoline). The emulsion now formed in only two sequences of stirring.

- 5 c) Repeat (of a) except that 20cc of water solution of Q2 (1 g/l H₂O) was added to 80cc Gasoline B containing S1 (3.75 g/l gasoline). The emulsion now formed in only two sequences of stirring.

EXAMPLE 8

- 10 Change of viscosity and stability.

a) For a 25cc water solution Q2 (1.0 g/l H₂O) and 100cc Gasoline B containing S1 (3.75) g/l gasoline) the sequence of Example 7 c was followed. The emulsion has a viscosity of about 3 centistokes and left a lower
15 layer of .84cc in 6.0cc total in a centrifuge tube under about 200 x g for 5 minutes.

b) stirring of the sample in a) of four additional stirring sequences at about twice the stirring speed gave an emulsion viscosity of about 12 centistokes
20 and a centrifuge lower layer (same centrifuge conditions) of about 0.3 cc, i.e. higher viscosity and greater stability with increased rate of shear.

c) To a 20cc water solution of Q3 (1 g/l H₂O) was added 80cc Gasoline B containing S1 (3.75 g/l
25 gasoline). The stirring sequence to form an emulsion of the inverted type took 10 sequences of the stirring rate of b) above plus 6 sequences of a combination of that of



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a) and b) above. With four additional sequences of stirring (after inversion) at the speed of b) above the viscosity of the emulsion was about 25 centistokes, with a centrifuge lower layer of about .48cc in 6cc total.

5 d) For the same composition as in c) above except that 20cc Q3 solution was replaced by 10cc Q2 solution and 10cc Q3 solution. A viscosity of 13 centistokes and a centrifuge lower layer of about .48cc in 6cc total was obtained. The emulsion was formed in
10 only three sequences of the stirring rate of b) above. This shows the synergistic effect of Q2 on rate of emulsion formation and Q3 on viscosity.

e) To 25cc solution of 1:1 Q1 and Q3 and one liter of water (1g/l H₂O) each was added 75cc S1
15 (3.75 g/l gasoline A). This solution was stirred at five times the stirring rate of Example 7 a) to produce an emulsion with a viscosity of about 50 centistokes and a centrifuge sedimentation of about .12cc. This sample was allowed to stand in a flask and showed no
20 appreciable separation for three months, after which about 0.1cc of water separated from about 100cc of emulsion over an additional month. This correlates the short term stability centrifuge test with long term stability, showing that both viscosity and lower
25 layer formation must be used to establish stability, for this emulsion. This shows that the stability of d) above is greater than c) although the centrifuge lower



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layer formation is the same.

EXAMPLE 9

Addition of Q material improves stability.

- a) A composition of 20cc H₂O and 80cc gasoline
5 B containing S1 (3.75 g/l) with stirring as in Example 8
b) gave an emulsion in 9 stirring sequences. Four more
similar stirring sequences gave an emulsion with a vis-
cosity of about 4 centistokes and a centrifuge lower
layer of .54cc in 6cc.
- 10 b) This experiment is the same as a) above
except that 20c water solution of Q2 (1g/l H₂O) replaced
the 20cc H₂O. A viscosity of about 8 centistokes and a
centrifuge lower layer of .54cc in 6cc were obtained.
This increase in viscosity with the Q material shows
15 increased stability over no use of Q material as in a)
above. See remarks at end of Example 8 e).

EXAMPLE 10

Q's have greatest effect with low concentration
of S's

- 20 a) To 30cc H₂O was added 120cc of gasoline B
containing S1 (50 g/l) and following two sequences of
stirring as in Example 7 a) a low internal phase ratio
(water in gasoline) was formed. With this composition a
viscosity of about one centistoke and a zero centrifuge
25 lower layer was obtained.*

**With this type of emulsion zero centrifuge lower layer
formation gave about 1.5% water layer in 7 days for long
term stability.

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b) Experiment a) above was repeated with 30cc water solution of Q1 (1 g/l H₂O) replacing the 30cc H₂O. The same type emulsion with the same viscosity and lower layer were obtained as in a) above. This Example compared with Examples 7, 8 and 9 shows that Q's are most effective with low concentrations of S materials in producing high internal phase ratio emulsions and changing viscosity and thus stability.

EXAMPLE 11

10 Effect of alcohols, salts H₂O/gasoline (Ratio).

a) A composition of 20cc water solution Q₂ (.34 g/l H₂O) and 80cc gasoline B (S1 solution concentration grams/l gasoline B) with 3 minutes of uninterrupted magnetic stirring gave an emulsion with a viscosity of about 4 centistokes and centrifuge lower layer of about .7cc in 6cc.

b) With the same composition as in a) above plus 1.0cc methanol, only 30 seconds were required to form an emulsion with a viscosity of about 3 centistokes and centrifuge lower layer of .9cc in 6cc.

c) With the same composition as in a) except that 1.2 g of S1 was added to the gasoline and the concentration of Q₂ was 1 g/l H₂O an emulsion was produced in 60 seconds of uninterrupted stirring that gave a viscosity of about 7 centistokes and a centrifuge lower layer of about .14cc in 6cc.

d) With the same composition as in c) above



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plus 1.0cc methanol only 15 seconds was required to produce an emulsion with a viscosity of about 3 centistokes and a centrifuge lower layer of about .8cc -- comparing a) with b) and c) with d) shows that methanol decreased the time of emulsification, decreases the emulsion viscosity, and decreases the stability.

e) A composition 10cc of water solution, Q2 (.34 g/l H₂O and 90cc gasoline B containing S1 (3.75 g/l) required five minutes of uninterrupted magnetic stirring to give an emulsion of with a viscosity of about 16 centistokes and a centrifuge lower layer of about .3cc in 6cc.

f) The same composition as in a) was used with the addition of 0.55cc CaCl₂ (2g/100cc H₂O) and it was not possible to produce an emulsion.

g) A composition of 30cc water solution Q2 (.34 g/l H₂O) and 70cc gasoline B containing S1 (3.75 g/l G25b) required 2 minutes of stirring to produce an emulsion with a viscosity of about 3 centistokes and a centrifuge lower layer of about 1.1 cc in 6cc.

h) A composition of 20cc water solution Q2 (1 g/l H₂O) 80cc gasoline B containing S1 (3.75 g/l) formed an emulsion, after 4 stirring sequences (as in Example 7a). This emulsion gave a viscosity of about 3 centistokes and gave a centrifuge lower layer of about .19cc in 6cc.

i) Decreasing the quantity of Q2 in h) above to 18cc and increasing the quantity of NaCl to 2cc

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prevented the formation of an emulsion. Comparing
2) with f) and h) with i) shows that salt concentration
can prevent a high internal phase ratio emulsion from
forming. Comparing e) with g) shows that increased
5 water phase gives an emulsion of this composition with
decreased viscosity and stability.

EXAMPLE 12

Tests with Q4, S2, S3, S4, S9

a) A composition of 20cc water solution Q4
10 (1 g/l H₂O) and 80cc S1. (3.75 g/l required 15 stirring
sequences of the type in Example 7 a) and after an invert
emulsion was formed 4 additional stirring sequences were
added. This gave an emulsion with a viscosity of about
10 centistokes and a centrifuge lower layer of about .33
15 cc in 6cc.

b) The composition of a) above was changed
for water phase to 10cc water solution Q1 (1.5 g/l H₂O)
plus 10cc water solution Q4 (1 g/l H₂O). The invert
emulsion was now formed in 2 stirring sequences. The
20 viscosity remained at 10 centistokes and the centrifuge
lower layer changed to .42cc in 6cc. Comparing a) and
b) shows similar synergistic effects to that obtained
in Example 8 d).

c) A composition of 20cc water solution Q2
25 (1/g/l H₂O) plus 80 cc gasoline B solution S2 (3.75
g/l was stirred for 70 seconds in a magnetic stirrer at
about .6 maximum stirring rate to produce an emulsion



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of the high internal phase ratio type. After an additional 30 seconds of stirring the emulsion had a viscosity of about 8 centistokes and a centrifuge lower layer of about .8cc in 6cc. In the following example

5 NaCl is used to prevent a high internal phase ratio emulsion from forming, so that the following three examples are of the low internal phase ratio type (water in hydrocarbon). In all cases maximum stirring speed of the magnetic stirrer was used. When a Warning Blender was

10 used it was found that the lower layer supernate interface (after centrifuging) centrifuging was less apparent. In all cases the viscosity of the emulsion was about 1.0 centistoke in the following three tests.

d) Composition: 3cc NaCl-water solution

15 (2g/100cc H₂O plus 14cc Q1 water solution (1.5 g/l H₂O) plus 14cc Q3 water solution (1 g/l H₂O) plus 90cc gasoline solution B (3.75 g/l gas b) gave zero centrifuge lower layer in 6cc and no water separation in seven weeks on standing.

20 e) Composition: 18cc H₂O plus 5cc water solution Q2 (1 g/l H₂O) plus .75cc S4 as is plus 1.5cc S3 as is 72cc gasoline B gave same centrifuge results as d) above.

f) Composition: 3.5cc water solution Q1 (1.5 g/l H₂O) plus 3.5cc water solution Q3 (1 g/l H₂O) plus 1.0cc S4 plus 1.5cc S3 plus 87cc gasoline B gave a centrifuge lower layer of about .06cc in 6cc.



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g) An invert emulsion was formed with 10cc water solution Q1 (.5 g/l H₂O) plus 90cc Angolan crude (containing 4 g sl/l crude). Less than 3cc of H₂O separated in 6 days.

5 h) A high internal phase ratio material was prepared with 9cc water solution Q1 (1.5 g/l H₂O) plus 50 cc # 2 oil (with 4g sl/l #2 oil) and stirring in a magnetic stirrer at 1/5 and 3/5 full scale. With the addition of an additional 40cc of #2 oil (with same
10 concentration of sl) the emulsion remained stable.

i) An emulsion of the type in H) above was made with 5cc water solution Q1 (1.5 g/l H₂O) plus 5cc water solution Q3 (1 g/l H₂O) plus 40cc #2 oil (with .25 S9) and the same stirring sequence.

15 This emulsion was broken with the addition of 40cc more of #2 oil and stirring. The emulsion was reformed with the further addition of .25 g of S9 with additional stirring. This emulsion was stable, with no water separation, for more than 19 days.

20 j) A stable coal-oil-water slurry was prepared with 5cc water solution Q1 (1.5 g/l H₂O) plus 5cc water solution Q3 (1 g/l H₂O) plus 11cc #6 oil (viscosity of 126 Furol at about 120°F) plus 0.5cc S9 plus 80 g Bituminous coal (-200 mesh, #6 Illinois).

25 Preparation was by hand for the first 60 g of coal and was stirred (600 r.p.m.) for the 80 grams of coal, with a glass stirrer, while the material was elevated in temperature of about 130°F, for 14 minutes of stirring.



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The slurry was then placed in a sole plastic syringe for sectioning at a later date, to determine settling.

EXAMPLE 13

a) Ten cc of H₂O was mixed with 100cc of #6
5 oil (126 Furol at 120°F) with a glass stirrer at about
600 r.p.m. for 5 minutes. When 60cc of this oil (no
water) is passed through a reference funnel at 23°C
it took 300 seconds to obtain a thin fulament of oil
and an additional 30 seconds before the end of the
10 pour. With the water addition the oil drained from
the side of a glass graduate at 23°C, in about 1.0
hour.

b) A composition and procedure described in
a) about was followed except that the 10cc of H₂O was
✓ 15 replaced by a water solution of 1 to 1 Q1 and Q3, with a
concentration of 1.5 g/l H₂O for Q3, plus about .3 g of
S9. The funnel test gave 25 seconds to filament and an
additional 30 seconds to end of pour. The separation
from the walls of the glass container took about 1.0
20 seconds (at 23°C); for about 90% of the poured material.
Parts a) and b) demonstrate that the addition of Q and
S materials change the pour ability of #6 oil, radically.

EXAMPLE 14

A composition of 3cc H₂O plus a 7cc H₂O solution
25 of Q1 (1.5 g Q1 / 1 H₂O) plus 91.5 cc of gasoline B plus
0.5cc S9, was formed in a Waring blender operating at
1/2 full speed for 5 minutes. This composition and



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procedure produced a very stable low internal phase ratio emulsion of water in gasoline. Less than 0.1cc in 90cc of a viscous water layer was deposited at the bottom of the containing cylinder.

- 5 Although the present invention has been disclosed with emphasis upon hydrocarbon and water mixtures with coal combustibles or non-combustibles or as involving water or coal or oil and coal, it is contemplated that the agent and the high molecular weight material
- 10 will achieve stable mixtures involving other materials or facilitate the transportation thereof.

- Also, even the hydrocarbon water mixture or other mixtures or the present invention can be readily transported or held in stable condition for purposes of
- 15 the combustion in the classical sense. For instance, the product of the invention can be used in the petrochemical industry where the mixture can be separated into components and such components utilized for their chemical or other value.

- 20 The present invention is also useful in maintaining the stability of a mixture of 90% gasoline and 10% alcohol, known as gasahol. Whenever water (from rainfall or otherwise) enters a tank of gasahol, it has been found that the water will tend to draw the alcohol
- 25 out of the gasahol solution. With the passage of time, the quantity of alcohol and water solution will accumulate at the bottom of a tank while gasoline (without



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water) goes to the top of the tank. This set-up will provide poor engine performance if the alcohol-water at the bottom of the tank is eventually drawn by the gasoline pump for combustion purposes into the engine. With the present invention, stability of the gasahol is maintained at all times, even when the water gets into the tank since water will not hinder the gasoline-alcohol mixture that is stabilized with the addition of a Q-S pair. Clearly, the present invention is operative even where the relative presence of alcohol is greatly increased up to and beyond the point where alcohol is present in an amount greater than the gasoline.

Without further elaboration the foregoing will so fully illustrate our invention that others may, by applying current or future knowledge, readily adapt the same for use under various conditions of service.



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What is claimed as the invention is:

1. In a mixture of a hydrocarbon and water, the improvement comprising achieving a very stable mixture above the freezing temperature of the mixture through the addition without a severe mixing action of a relatively low molecular weight agent and a high molecular weight material with at least one of said agent and material having an affinity between the water and the hydrocarbon.
2. The mixture of Claim 1 wherein the hydrocarbon is a liquid.
3. The mixture of Claim 2 wherein the hydrocarbon is gasoline.
4. The mixture of Claim 2 wherein the hydrocarbon is heating oil.
5. The mixture of Claim 2 with the further addition of coal.
6. The mixture of Claim 2 with the further addition of lignite.
7. The mixture of Claim 2 wherein the hydrocarbon is crude oil.
8. The mixture of Claim 2 used as a pour point depressant.
9. The mixture of Claim 2 used for transportation purposes.
10. The mixture of Claim 2 wherein the agent is sodium salt of dioctylsulfosuccinnic acid.



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11. The mixture of Claim 2 wherein the agent is sodium salt of decylbenzenesulfonic acid.
12. The mixture of Claim 2 wherein the agent is calcium dodecyl benzene sulfonate and alkyl phenoxy polyoxyethylene ethanol.
13. The mixture of Claim 2 wherein the agent is octylphenoxypolyethoxy ethanol.
14. The mixture of Claim 2 wherein the agent is alkylamine dodecyl benzene sulfonate.
15. The mixture of Claim 2 wherein the high molecular weight material is swellable poly (acrylamide/sodium acrylate) partially crosslinked.
16. The mixture of Claim 2 wherein the high molecular weight material is swellable hydrolyzed starch polyarylonitrile graft copolymer.
17. The mixture of Claim 2 wherein the high molecular weight material is water soluble high molecular weight polyacrylic acid in the completely neutralized form.
18. The mixture of Claim 2 wherein the high molecular weight material is polyoxyethylene having a molecular weight in excess of 500,000.
19. The mixture of Claim 2 wherein the agent is sodium salt of dioctylsulfosuccinnic acid and the high molecular weight material is a mixture of swellable poly (acrylamide/sodium acrylate) partially crosslinked and water soluble high molecular weight polyacrylic acid



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in the completely neutralized form.

20. The mixture of Claim 19 with the further addition of coal.

21. The mixture of Claim 2 wherein the agent is sodium salt of dioctylsulfosuccinnic acid and the high molecular weight material is a mixture of swellable hydrolyzed starch polyacrylonitrile graft copolymer.

22. The mixture of Claim 2 wherein the agent is sodium salt of dioctylsulfosuccinnic acid and the high molecular weight material is a mixture of water soluble high molecular weight polyacrylic acid in the completely neutralized form.

23. In a mixture of coal and water, the improvement comprising achieving a very stable mixture above the freezing temperature of the mixture through the addition without a severe mixing action of a relatively low molecular weight agent and a high molecular weight material with a least one of said agent and material having an affinity with said water.

24. The mixture of Claim 23 with the further addition of liquid hydrocarbon with one of said agent and material having affinity between the water and the hydrocarbon.

25. In a mixture of coal and oil, the improvement comprising achieving a very stable mixture above the freezing temperature of the mixture through the addition without severe mixing action of a relatively

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low molecular weight agent and a high molecular weight material with at least one of said agent and material having an affinity with said oil.

26. A stabilizer for a mixture above the freezing temperature, having at least one ingredient, said stabilizer comprising a relatively low molecular-weight agent and a high molecular weight material with at least one of said agent and material having an affinity for said ingredient to achieve a stable mixture, said mixture being achieved without a severe mixing action.

27. In a mixture of a hydrocarbon and water, the improvement comprising achieving a very stable mixture above the freezing temperature of the mixture through the addition without a severe mixing action of a relatively low molecular weight agent and a high molecular weight material wherein the molecular weight of said material is at least 500,000.

28. The mixture of Claim 27 wherein said relatively low molecular weight agent has a molecular weight between 225 and 10,000.

29. The mixture of Claim 28 wherein said relatively low molecular weight agent has a molecular weight between 272 and 690.

30. In a process of facilitating the transportation through piping of substances, said process comprising treating the internal surface of said piping with a high molecular weight material having a molecular



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weight of at least 500,000.

31. The process of Claim 30 wherein the treating of the internal surface of said piping involves a pretreating step.

32. The process of Claim 30 wherein the treating of the internal surface of said piping involves incorporating said material into said substances.

33. In a process of facilitating the transportation through piping of substances, said process comprising treating the internal surface of said piping with a silicate solution.

34. The process of Claim 33, wherein there is added to said silicate prior to treatment a high molecular weight material and a low molecular weight agent.

35. In a gasoline mixture, the improvement comprising adding an amount of high molecular weight material and a low molecular weight agent sufficient for stabilization in the presence of water.

36. A method of achieving stability in a coal oil mixture comprising adding to said mixture a sufficient amount of at least one high molecular weight material and at least one low molecular weight agent.

37. The method of Claim 36 involving a coal oil water mixture.

38. The process of Claim 1 wherein said high molecular weight material is irradiated polymerized



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sodium carboxymethylcellulose.

39. For agricultural use involving a mixture of a hydrocarbon, an agriculturally active agent and water, the improvement comprising achieving a very stable mixture above the freezing temperature of the mixture through the addition without a severe mixing action of a relatively low molecular weight agent and a high molecular weight material with at least one of said agent and material having an affinity between the water and the hydrocarbon.

40. A method of formulating a hydrocarbon, an agriculturally active agent and water comprising adding thereto a relatively low molecular weight agent and a high molecular weight material with at least one of said agent and material having an affinity between the water and the hydrocarbon, and imparting a mixing agent to achieve a very stable mixture.



AMENDED CLAIMS

(received by the International Bureau on 6 July 1981 (06.07.81))

1. A mixture comprising a hydrocarbon and water
characterised by the presence of a relatively low molecular weight hydrophilic-lipophilic agent and a high molecular weight water soluble or water-swella-
ble material, at least one of which has an affinity to both the water and the hydrocarbon.
2. A mixture according to Claim 1, characterised in that
the agent has a molecular weight from about 225 to about 1000.
3. A mixture according to Claim 2, characterised in that
the molecular weight is between 272 and 690.
4. A mixture according to Claim 2 or 3, characterised in that the agent is the sodium salt of dioctylsulphosuccinic acid, or decylbenzenesulphonic acid; calcium dodecyl benzene sulphonate or alkyl phenoxy polyoxyethylene ethanol; octylphenoxypolyethoxy, or an alkylamine dodecyl benzene sulphonate.
5. A mixture according to Claim 1, 2, 3 or 4, characterised in that the high molecular weight material has a molecular weight in excess of 500,000.
6. A mixture according to Claim 5, characterised in that



the material is swellable poly (acrylamide/sodium acrylate) partially crosslinked, swellable hydrolyzed starch polyacrylonitrile graft copolymer, water soluble high molecular weight polyacrylic acid in the completely neutralized form.

7. A mixture according to Claim 5, characterised in that the material is irradiated polymerised sodium carboxy methyl cellulose, polybutadiene, polyvinyl acetate or polystyrene.
8. A mixture according to any preceding claim, characterised in that the agent is sodium salt of dioctylsulphosuccinnic acid and the high molecular weight material is a mixture of swellable poly (acrylamide/sodium acrylate) partially crosslinked and water soluble high molecular weight polyacrylic acid in the completely neutralized form.
9. A mixture according to any preceding Claim, characterised in that the hydrocarbon is a liquid or solid or both.
10. A mixture according to Claim 9, characterised in that the hydrocarbon is selected from one or more of gasoline, heating oil, crude oil, coal, lignite or gasohol.



11. A mixture according to any preceding Claim,
characterised in that silicate solution is additionally present.
12. A mixture according to any preceding Claim,
characterised in that a plant growth regulator is present.
13. A mixture according to Claim 12, characterised in that the plant growth regulator is 2,4-D.
14. A method of making a mixture according to any preceding Claim, characterised by mixing the ingredients at room temperature with gentle mixing for a period not exceeding 15 minutes.
15. A method according to Claim 14, characterised in that the formed mixture is pumped along a pipeline to an end destination.
16. A method according to Claim 15, characterised in that the interior surface of the pipeline is coated with the material before pumping is started.
17. A method according to Claim 15, characterised in that the interior of the surface of the pipeline is coated with a silicate solution.



EDITORIAL NOTE

The applicant failed to renumber the amended claims in accordance with Section 205 of the Administrative Instructions.

In the absence of any specific indication from the applicant as to the correspondence between original and amended claims, these claims are published as filed and as amended.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 80/01760

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. 3 C10L 1/32, 1/28; F17D 1/16, 1/17; F16L 9/00, 9/14; *		
US. CL. 44/51, 62; 137/13; 138/146; 252/309, 312 * 801J 13/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
US	44/51, 62; 137/13; 138/146; 252/309, 312	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT 14		
Category *	Citation of Document, 15 with Indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
X, A	FR, A1, 315, 131, Published, 10 December 1962, Mohier	1-3, 8, 9, 26, 30, 32, 35, 36, 39, 40
X, A	US, A3, 852, 234, Published, 03 December 1974, Venema	1, 2, 10-22, 26-39
X	US, A4, 022, 731, Published, 10 May 1977, Schmitt	1, 2, 4-7, 17, 20
X, L	US, A3, 943, 060, Published, 09 March 1976, Martin et al	30-32
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* Special categories of cited documents: 16 "A" document defining the general state of the art "E" earlier document but published on or after the international filing date "L" document cited for special reason other than those referred to in the other categories "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but on or after the priority date claimed "T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention "X" document of particular relevance		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search *	Date of Mailing of this International Search Report *	
APRIL 21, 1981	05 MAY 1981	
International Searching Authority *	Signature of Authorized Officer, 19	
ISA/US	RAYMOND K. COVINGTON	

Form PCT/ISA/210 (second sheet) (October 1977)

United States Patent [19]
Rivas et al.



US005354504A

[11] Patent Number: 5,354,504

[45] Date of Patent: Oct. 11, 1994

[54] METHOD OF PREPARATION OF
EMULSIONS OF VISCOUS HYDROCARBON
IN WATER WHICH INHIBITS AGING

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Venezuela

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[21] Appl. No.: 746,985

[22] Filed: Aug. 19, 1991

[51] Int. Cl.⁵ B01J 13/00; F17D 1/16

[52] U.S. Cl. 252/314; 252/312;
137/13; 44/300

[58] Field of Search 252/312, 314, 311, 311.5;
137/13; 44/300

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production and handling of extra-heavy crude oil and
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Primary Examiner—Robert L. Stoll

Assistant Examiner—Daniel S. Metzmaier

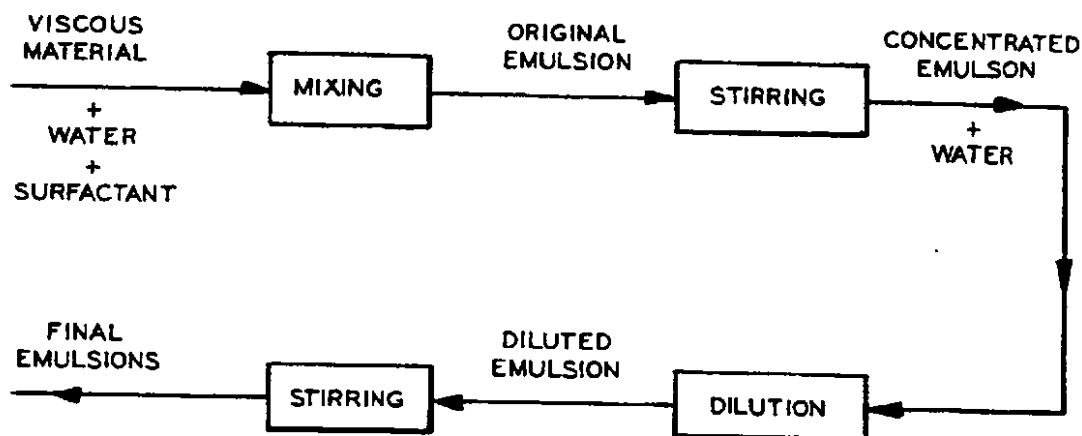
Attorney, Agent, or Firm—Bachman & LaPointe

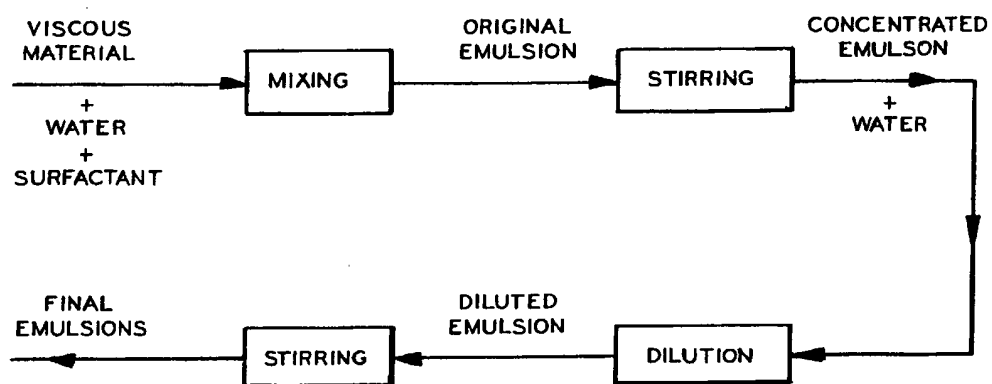
[57]

ABSTRACT

A method for the preparation of a hydrocarbon in water
emulsion from viscous hydrocarbons wherein aging of
the emulsion over time is substantially eliminated com-
prises forming a concentrated emulsion characterized
by a water content of less than or equal to 15%/wt. and
an average oil droplet size of less than or equal to 4
microns and thereafter forming a final emulsion by
diluting the concentrated hydrocarbon in water emul-
sion with water so as to obtain a water content of less
than or equal to 30%/wt. and stirring said diluted emul-
sion so as to obtain a final hydrocarbon in water emul-
sion having an average oil droplet size of greater than or
equal to 15 microns.

17 Claims, 2 Drawing Sheets



**FIG -1**

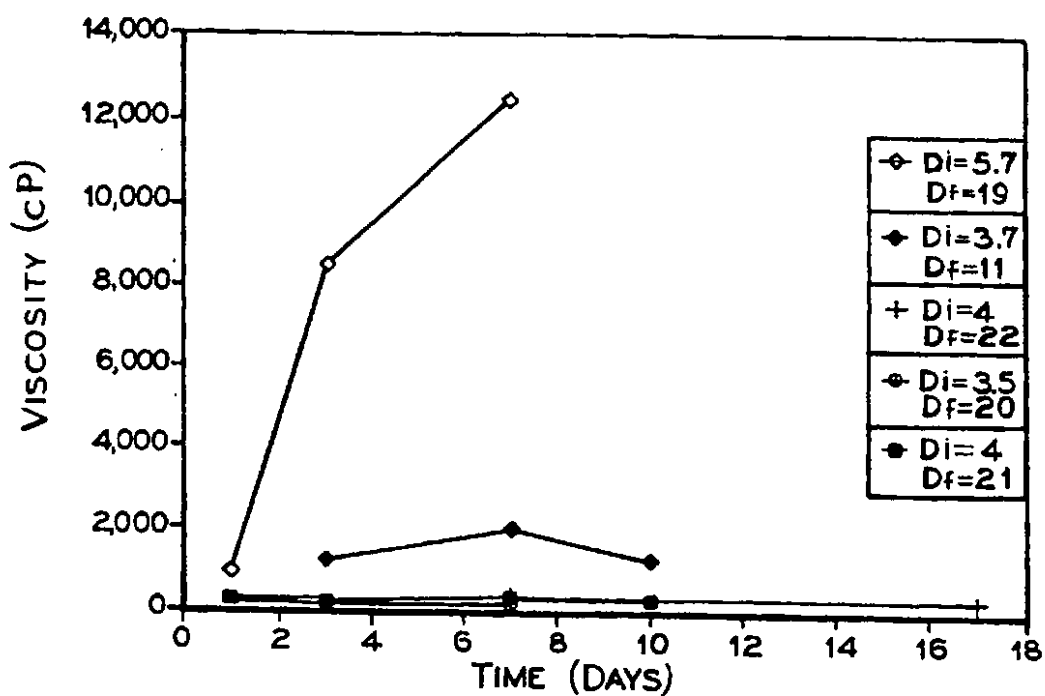


FIG-2

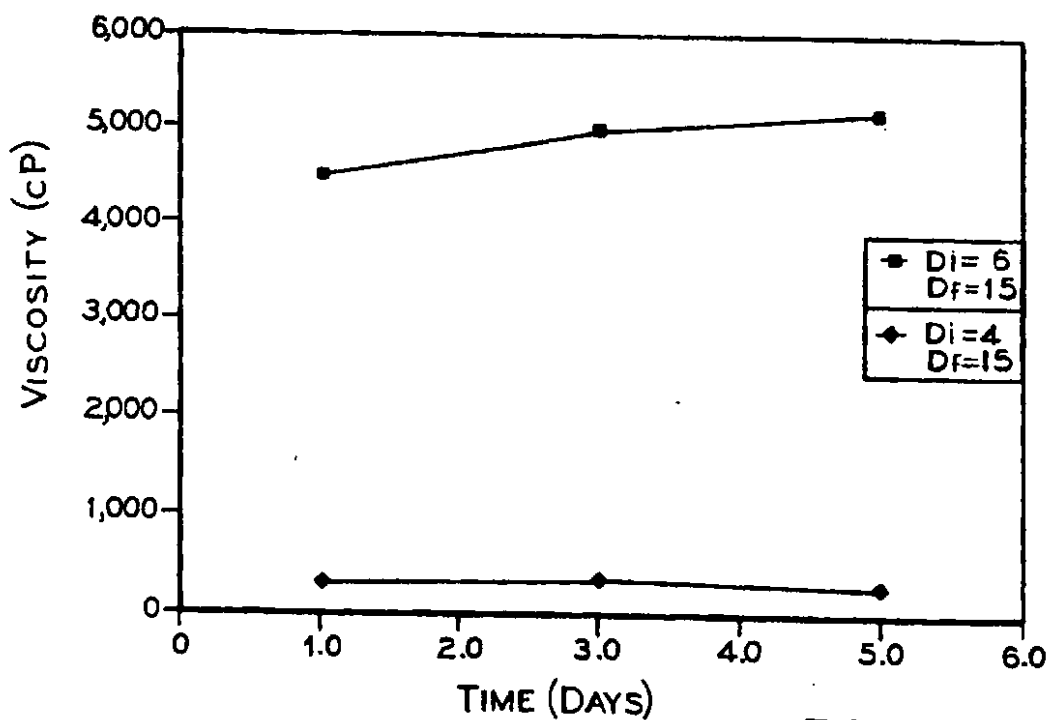


FIG-3

METHOD OF PREPARATION OF EMULSIONS OF VISCIOUS HYDROCARBON IN WATER WHICH INHIBITS AGING

BACKGROUND OF THE INVENTION

The present invention is drawn a method for the preparation of a hydrocarbon in water emulsion from viscous hydrocarbons and, more particularly, a method for the preparation of low-viscosity hydrocarbon in water emulsions from viscous hydrocarbons wherein aging of the emulsion over time is substantially eliminated.

The viscous hydrocarbons (below 12° API gravity) found in Canada, the Soviet Union, the United States, China, and Venezuela, are liquids having viscosities running from 10,000 to 500,000 centipoise at room temperature. Normally, these viscous hydrocarbons are produced by mechanical pumping alone, mechanical pumping combined with steam injection, and through mining techniques. To make hydrocarbons of this kind more commercially valuable, it is necessary to develop methods to increase the effectiveness and profitability of their transportation and storage thereby facilitating their subsequent use as raw materials in the derivation of other products or in other applications. Processes have been conceived to modify these hydrocarbons so as to change them into a pumpable form and make it possible to move them through conventional pipes. Among the most common processes is that of forming emulsions of these hydrocarbons in water. The emulsions have much lower viscosity than the hydrocarbon alone and thus can be pumped at a faster speed through the pipe lines with conventional pumping equipment.

The aforesaid emulsions are prepared using surfactants, which can be cationic, anionic, and/or non-ionic. Their preparation involves a large number of variables, both physical-chemical (covering the formulation of the emulsion) and mechanical (relating to the method and speeds of stirring). These variables are very important, since the stability of the emulsion, that is, that their component phases do not separate out and that their viscosity remains constant over time, depends upon these variables.

Several methods have been proposed for forming emulsions of hydrocarbons in water using chemical additives, thereby reducing the viscosity of the hydrocarbons so as to make them transportable.

Typical processes are described in U.S. Pat. Nos. 3,380,531; 3,467,159; 3,487,844; 3,006,354; 3,425,429; 3,467,195; 3,519,006; 3,943,954; 4,099,537; 4,108,193; 4,239,052; 4,249,554; 4,627,458; and 4,795,478. They involve the use of sodium or ammonium hydroxide, non-ionic, anionic, and cationic surfactants, or combinations thereof.

The foregoing methods produce stable emulsions from the point of view of the coalescence of their phases. However, a problem which has not been resolved to date is that of controlling or eliminating the phenomenon of aging which affects these emulsions. By aging is meant the progressive increase in the viscosity of the emulsion over time. One technique used to prevent aging involves the addition of electrolytes which involves an additional cost in the process of preparation of the emulsions.

Naturally, it would be highly desirable to provide a method for preparation of hydrocarbon in water emul-

sions from viscous hydrocarbons wherein aging of the emulsion over time is substantially eliminated.

Accordingly, it is the principle object of the present invention to provide a method for the preparation of hydrocarbon in water emulsions from viscous hydrocarbons wherein the aging of the emulsion over time is substantially eliminated.

It is the principle object of the present invention to provide a method as aforesaid wherein the final emulsion exhibits a viscosity of less than or equal to 1500 centipoise at 80° F.

It is a further object of the present invention to provide a method for the preparation of hydrocarbon in water emulsions as aforesaid wherein the average oil droplet size in the final emulsion product is greater than or equal to 15 microns.

It is a still further object of the present invention to provide a method for the preparation of hydrocarbon in water emulsions from viscous hydrocarbons as aforesaid wherein the hydrocarbon is the natural occurring crude, tar or other natural occurring hydrocarbon or residual fuel oil characterized by a viscosity of greater than 100 centipoise at 122° F. and an API gravity of greater than or equal to 16° API.

Further objects and advantage of the present invention will appear hereinbelow.

SUMMARY OF THE INVENTION

The present invention is drawn to a method for the preparation of a hydrocarbon in water emulsion from viscous hydrocarbons and, more particularly, a method for the preparation of low-viscosity hydrocarbon in water emulsions from viscous hydrocarbons wherein aging of the emulsion over time is substantially eliminated.

The method in accordance with the present invention comprises the steps of first forming a concentrated emulsion by admixing a viscous hydrocarbon with emulsifier and water so as to obtain a water content in an amount of less than or equal to 15%/wt. The aforesaid mixture is thereafter heated to a temperature of between 120° F. and about 200° F. and thereafter the heated mixture is stirred under controlled conditions so as to obtain a concentrated hydrocarbon in water emulsion having an average oil droplet size of less than or equal to 4 microns. After obtaining the concentrated emulsion, a final emulsion is prepared by first diluting the concentrated hydrocarbon in water emulsion with water so as to obtain a water content of less than or equal to 30%/wt. The diluted mixture is thereafter heated to a temperature of between 140° F. to about 220° F. The heated diluted mixture is then stirred under controlled conditions so as to obtain a final hydrocarbon in water emulsion having an average oil droplet size of greater than or equal to 15 microns wherein the viscosity of the final emulsion is less than or equal to 1500 centipoise at 1 s⁻¹ and 80° F.

The hydrocarbon in water emulsion produced by the method as aforesaid results in an emulsion which is not only stable but which is substantially impervious to the aging phenomena heretofore exhibited by hydrocarbon in water emulsions produced by prior art processes.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing the steps for preparing a hydrocarbon in water emulsion according to the method of the present invention;

FIG. 2 is a graph of five curves showing the effect of oil droplet size on the aging of hydrocarbon in water emulsions prepared in accordance with Example II;

FIG. 3 is a graph of two curves showing the effect of oil droplet size on the aging of hydrocarbon in water emulsions prepared in accordance with Example IV.

DETAILED DESCRIPTION

The method of the present invention allows for the preparation of hydrocarbon in water emulsions from viscous hydrocarbons wherein aging of the emulsions over time is substantially eliminated.

FIG. 1 is a schematic diagram showing the steps for preparing hydrocarbon in water emulsion from a viscous hydrocarbon in accordance with the method of the present invention. The process of the present invention is particularly suitable for viscous hydrocarbons having the following physical and chemical properties: ° API gravity of between 1 and 16; viscosity at 122° F. of between 100,000 and 500,000 centipoise; viscosity at 210° F. of between 10,000 and 16,000 centipoise; asphaltene content of between 5 and 25%/wt.; resin content of between 3 and 30%/wt.; carbon content of between 78.2 and 85.5%/wt.; hydrogen content of between 9.0 and 10.8%/wt.; oxygen content of between 0.25 and 1.1%/wt.; nitrogen content of between 0.5 and 0.7%/wt.; sulfur content of between 2.0 and 4.5%/wt.; vanadium content of between 50 to 1000 ppm; nickel content of between 20 to 500 ppm; iron content of between 5 to 100 ppm; sodium content of between 10 to 500 ppm; and ash content of between 0.55 and 0.3%/wt. The viscous hydrocarbons may be in the form of heavy crude oils, naturally occurring bitumens, naturally occurring tars, heavy residuals, and the like.

In accordance with the method of the present invention, the non-aging hydrocarbon in water emulsion is prepared by first forming a concentrated emulsion. With reference to FIG. 1, the concentrated hydrocarbon in water emulsion is formed by admixing a viscous hydrocarbon with water and an emulsifying additive. The amount of water admixed with the hydrocarbon and emulsifying additive is such as to insure that the water content in the concentrated emulsion is less than or equal to 15%/wt. water. The emulsifying additive is added in an amount of between 0.1 and 5.0%/wt., preferably between 0.1 and 1.0%/wt., based on the total weight of the concentrated hydrocarbon in water emulsion.

The preferred emulsifying additive for use in the method of the present invention comprises a mixture of either a non-ionic surfactant or anionic surfactant with a phenol-formaldehyde-ethoxylated resin. The phenol-formaldehyde-ethoxylated resin is combined with the surfactant in an amount of between 1 to 10%/wt. preferably 1 to 5%/wt. based on the total weight of the emulsifying additive.

Useful non-ionic surfactants for use in the method of the present invention include ethoxylated alkyl phenol, ethoxylated alcohols, and esters of ethoxylated sorbitan compounds. Preferred non-ionic surfactants should have a hydrophylic-lipophylic balance (HLB) of greater than 13. Preferred non-ionic surfactants include alkyl phenol ethoxylates. Particularly useful anionic surfactants include alkyl arylsulphonates and alkyl arylsulfates and surfactants derived from long-chain carboxylic acids. Preferred anionic surfactants include those having a HLB of greater than 13, for example, ammonium alkylaryl sulphonates such as dodecyl ben-

zenesulphonate. The phenol-formaldehydeethoxylated resin-preferably has from 3 to 7 ethoxy units.

The admixed viscous hydrocarbon, water and emulsifying additive is then heated to a temperature of about between 120° F. to 200° F. and the heated mixture is thereafter stirred under controlled conditions so as to form a concentrated hydrocarbon in water emulsion having an average oil droplet size of less than or equal to 4 microns. In accordance with the present invention, the heated mixture is stirred in a high-speed mixer at an rpm of less than or equal to 2000 rpm and, preferably, between 1000 and 1500 rpm.

The concentrated hydrocarbon in water emulsion is then diluted with water so as to obtain a water content of between 20 to 30%/wt., preferably 28%/wt. The diluted mixture is then heated to a temperature of between about 140° F. and 220° F., preferably between 180° F. and 220° F. The heated diluted emulsion is then subjected to shearing in a high-speed mixer at speeds of up to 4500 rpm and preferably between 3500 and 4500 rpm so as to obtain a final hydrocarbon in water emulsion product having an average oil droplet size of greater than or equal to 15 microns and a viscosity of less than or equal to 1500 centipoise at 80° F.

The non-aging hydrocarbon in water emulsion formed in accordance with the method of the present invention comprises preferably from about 70 to 80%/wt. oil, from about 20 to 30%/wt. water, from about 0.1 to 5%/wt. of an emulsifying agent, an average oil droplet size of greater than or equal to 15 microns, and a viscosity of less than or equal to 1500 centipoise at 1 s and 80° F. The aging factor of the non-aging hydrocarbon in water emulsion is an average change in viscosity of less than 100 centipoise per month and preferably 100 centipoise per year. By aging factor is meant the change in viscosity at a given temperature over time. In accordance with the preferred embodiment of the present invention the non-aging hydrocarbon contains an emulsifying agent which comprises a mixture of either a non-ionic surfactant with a phenol-formaldehydeethoxylated resin or an anionic surfactant with a phenol-formaldehyde-ethoxylated resin wherein the phenol-formaldehyde-ethoxylated resin is combined with the surfactant in an amount of between 1 to 10%/wt., preferably 1 to 5%/wt. based on the total weight of the emulsifying additive. The non-aging hydrocarbon in water emulsions produced in accordance with the method of the present invention substantially eliminate the aging phenomena which plague hydrocarbon in water emulsions formed by other known methods. The non-aging characteristics of the hydrocarbon in water emulsions formed by the method of the present invention will be made clear from the following illustrative examples.

EXAMPLE I

In order to demonstrate the effect of the method of the present invention for producing hydrocarbon in water emulsions wherein aging of the emulsion over time is substantially eliminated, a naturally occurring viscous hydrocarbon was admixed with water and an emulsifying additive. The naturally occurring viscous hydrocarbon was a Cerro Negro tar from the Orinoco Oil Belt region of Venezuela. The physical and chemical properties of the Cerro Negro tar employed in this example is set forth below.

Gravity API (60° F.)

8.4

-continued

Saturates %/wt.	11.8
Aromatics %/wt.	45.8
Resins %/wt.	30.9
Asphaltenes %/wt.	11.5
Acidity, mgKOH/g of bitumen	3.07
Total nitrogen ppm	5561
Sulfur %/wt.	3.91
Nickel ppm	105.9
Vanadium ppm	544.2

The emulsifying additive comprised a non-ionic surfactant in the form of an alkyl phenol ethoxylated compound sold under the trademark INTAN-100® which is a trademark of Intevep, S.A. and a phenol-formaldehydeethoxylated resin having 5 units of ethyl oxide. The emulsifying composition comprised 97%/wt. of the non-ionic surfactant and 3%/wt. of a phenol-formaldehyde-ethoxylated resin. The mixture comprised 93%/wt. of the Cerro Negro tar, 6.7%/wt. of distilled water, and 0.3%/wt. of the emulsifying composition described above. The mixture was heated to a temperature of 167° F. and slowly pre-mixed. The mixture was then stirred with a spiral palet at a speed of 1200 rpm to obtain a first concentrated emulsion. Four samples of the first concentrated emulsion were taken after stirring times of 2 min., 4 min., 4 min., and 4 min., respectively. The average diameter of the oil droplet size of the four samples of the first concentrated emulsion was measured and the results are set forth below in Table I.

TABLE I

Concentrated Emulsion		
Sample	Time, Minutes	Average Dia. Microns
1	2	8.6
2	4	3.8
3	4	3.9
4	4	3.5

Each of the four samples of the first concentrated emulsion were then diluted with distilled water so as to obtain a water content of 28%/wt. The diluted emulsion was then heated to a temperature of 176° F. and stirred at a speed of 4000 rpm. The four samples were stirred for a time of 1 min., 2 min., 3 min., and 4 min., respectively. The final cooled emulsions were stored at 0° F. for 24 hours and the average oil droplet diameter was measured as was the viscosity of each of the samples. Viscosity measurements were again taken after 48 hours. The results are set forth in Table II below.

TABLE II

Diluted Emulsion			Viscosity (cPs) at	
Sample	Time, Minutes	Average Dia. Microns	1 s ⁻¹ and 80° F. after	
			24 hrs.	48 hrs.
1	1	16	18,610	20,000
2	2	7	7,280	7,300
3	3	10	4,124	4,100
4	4	15	500	250

FIG. 2 demonstrates oil droplet diameter size in the concentrated emulsion and the final diluted emulsion has on the viscosity of the final emulsion. From Table II it can be seen that samples 2, 3, and 4 which had an

average oil droplet diameter of less than 4 microns do not show virtually any aging of the final emulsion product while sample 1 which had an average oil droplet diameter of 8.6 microns in the concentrated emulsion aged when formed to a final emulsion product. In addition, it can be seen that as the average oil droplet diameter increased in the final emulsion product of samples 2, 3, and 4 the final viscosity of the product was greatly reduced. Not only was the viscosity of the final diluted emulsions improved with increased oil droplet size, the non-aging characteristics of the emulsions likewise increased with an increase in oil droplet diameter size. This example clearly demonstrates the criticality of oil droplet diameter size in both concentrated emulsion and the final diluted emulsion in order to obtain a low viscosity non-aging hydrocarbon in water emulsion in the final emulsion product. From Table II it can be seen that it is preferred that the concentrated emulsion have an average oil droplet size of less than or equal to 4 microns and that the final emulsion product have an average oil droplet size of greater than or equal to 15 microns.

EXAMPLE II

Five additional samples were prepared following the same procedure as described above in Example I with only the time of stirring being varied so as to obtain different oil droplet diameter sizes in the concentrated emulsions and the final diluted emulsions. Table III below sets forth the average oil droplet diameter for the concentrated and diluted emulsions for each of the five samples.

TABLE III

Sample	Average Dia., Microns Concentrated Emulsion	Average Dia., Microns Diluted Emulsion
1	5.7	19
2	3.7	11
3	3.5	20
4	4.0	21
5	4.0	22

The samples were stored at 80° F. and the viscosity of the emulsions were measured at regular time intervals for ten days in order to determine the non-aging characteristics of the emulsions. The results are summarized in FIG. 2. As can be seen from FIG. 2, again initial oil droplet size in the concentrated emulsion is important for obtaining a non-aging hydrocarbon in water emulsion. In addition, it can be seen that final oil droplet diameter is important for obtaining low viscosity non-aging hydrocarbon in water emulsions.

EXAMPLE III

Example II was again repeated with the exception that the emulsifying composition was a mixture of 97%/wt. ammonium dodecylbenzenesulphonate and 3%/wt. of the same formaldehyde resin used in Example II. The average oil droplet diameter was again measured for each of the samples after the formation of the concentrated emulsion and the final diluted emulsion. The final diluted emulsions were again cooled to 80° F. and the viscosities were measured after 24 and 48 hours. The results are set forth below in Table IV.

TABLE IV

Sample	Average Dia. Microns Concentrated Emulsions	Average Dia. Microns Diluted Emulsions	Viscosity (cPs) at	
			1 s ⁻¹ after	
			24 hrs.	48 hrs.
1	4	15	600	8700

TABLE IV-continued

Sample	Average Dia. Microns Concentrated Emulsions	Average Dia. Microns Diluted Emulsions	Viscosity (cPs) at 1 s ⁻¹ after	
			24 hrs.	48 hrs.
2	5	8	7200	7700
3	8	15	8700	9300

Again, it is clearly seen the criticality of obtaining an oil droplet size in the concentrated emulsion of less than or equal to 4 microns in order to reduce the viscosity of the final hydrocarbon in water emulsion as well as the non-aging characteristics of the final hydrocarbon in water emulsion.

EXAMPLE IV

Two additional samples were prepared using the emulsifier composition of Example III and following the same procedure of Example II described above. The average oil droplet diameter size for the concentrated and diluted emulsions of each of the samples is set forth below in Table V.

TABLE V

Sample	Average Dia. Microns Concentrated Emulsion	Average Dia. Microns Diluted Emulsion
1	6	15
2	4	15

The emulsions were again cooled to 80° F. and the viscosities were measured after 1 day, 3 days, and 5 days. The behavior of the emulsions with storage time are summarized in FIG. 3. Again, it is clearly demonstrated that the oil droplet size as a concentrated emulsion is critical in obtaining a low viscosity, non-aging hydrocarbon in water emulsion.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

We claim:

1. A method for the preparation of a low viscosity, non-aging hydrocarbon in water emulsion from a viscous hydrocarbon wherein aging of the emulsion over time is substantially eliminated comprising the steps of:

(a) forming a concentrated emulsion by:

(1) admixing said viscous hydrocarbon with an emulsifying additive comprising a non-ionic surfactant, a phenol-formaldehyde ethoxylated resin in an amount of between 1 to 5%/wt. based on the total weight of the emulsifying additive and water wherein a water content is less than or equal to 15%/wt.;

(2) heating said mixture to a temperature of between about 120° F. to about 200° F.; and

(3) stirring said heated mixture under controlled conditions so as to obtain a concentrated hydrocarbon in water emulsion having an average oil droplet size of less than or equal to 4 microns;

(b) forming a final emulsion by:

(1) diluting said concentrated hydrocarbon in water emulsion with water so as to obtain a water content greater than the water content of the concentrated emulsion and less than or equal to 30%/wt.;

(2) heating said diluted mixture to a temperature of between about 140° F. to about 220° F.; and

(3) stirring said heated mixture under controlled conditions so as to obtain a final hydrocarbon in water emulsion having an average oil droplet size of greater than or equal to 15 microns wherein the viscosity of the final emulsion is less than or equal to 1500 centipoise at 1 s⁻¹ and 80° F.

2. A method according to claim 1 wherein said mixture is heated to a temperature of between 120° F. and 180° F. in step (a) (2).

3. A method according to claim 1 wherein said heated mixture is stirred at a speed of between 1000 to rpm in step (a) (3).

4. A method according to claim 1 wherein said diluted mixture is heated to a temperature of between about 180° F. to about 220° F. in step (b) (2).

5. A method according to claim 1 wherein said heated diluted mixture is stirred at a speed of between to 4500 rpm in step (b) (3).

6. A method according to claim 1 wherein said viscous hydrocarbon has the following physical and chemical properties: API gravity of between 1 and 16; viscosity at 122° F. of between 100,000 and 500,000 centipoise; viscosity at 210° F. of between 10,000 and 16,000 centipoise; asphaltene content of between 5 and 25%/wt.; resin content of between 3 and 30%/wt.; carbon content of between 78.2 and 85.5%/wt.; hydrogen content of between 9.0 and 10.8%/wt.; oxygen content of between 0.25 and 1.1%/wt.; nitrogen content of between 0.5 and 0.7%/wt.; sulfur content of between 2.0 and 4.5%/wt.; vanadium content of between 50 to 1000 ppm; nickel content of between 20 to 500 ppm; iron content of between 5 to 100 ppm; sodium content of between 10 to 500 ppm; and ash content of between 0.55 and 0.3%/wt.

7. A method according to claim 1 wherein said emulsifying additive is present in the (concentrated or final) emulsion in an amount of between 0.1 to 5%/wt. based on the total weight of the (concentrated or final) emulsion.

8. A method according to claim 1 wherein said phenol-formaldehyde ethoxylated resin is present in an amount of between 1 to 2%/wt. based on the total weight of the emulsifying additive.

9. A method according to claim 1 wherein said non-ionic surfactant has a hydrophilic-lipophilic balance of greater than 13 and said phenol-formaldehyde ethoxylated resin has from 3 to 7 ethoxy units.

10. A method according to claim 1 wherein said non-ionic surfactant is selected from the group consisting of ethoxylated alkyl phenol, ethoxylated alcohols, and esters of ethoxylated sorbitans compounds.

11. A method according to claim 1, wherein the water content of the final emulsion is between about 20%/wt. to about 30%/wt.

12. A method for the preparation of a low viscosity, nonaging hydrocarbon in water emulsion from a viscous hydrocarbon wherein aging of the emulsion over time is substantially eliminated comprising the steps of:

(a) forming a concentrated emulsion by:

(1) admixing said viscous hydrocarbon with an emulsifying additive comprising an anionic surfactant, a

- phenol-formaldehyde ethoxylated resin in an amount of between 1 to 5%/wt. based on the total weight of the emulsifying additive and water wherein a water content is less than or equal to 15%/wt.;
- (2) heating said mixture to a temperature of between about 120° F. to about 200° F.; and
- (3) stirring said heated mixture under controlled conditions so as to obtain a concentrated hydrocarbon in water emulsion having an average oil droplet size of less than or equal to 4 microns;
- (b) forming a final emulsion by:
- (1) diluting said concentrated hydrocarbon in water emulsion with water so as to obtain a water content greater than the water content of the concentrated emulsion and less than or equal to 30%/wt.;
- (2) heating said diluted mixture to a temperature of between about 140° F. to about 220° F.; and
- (3) stirring said heated mixture under controlled conditions so as to obtain a final hydrocarbon in water emulsion having an average oil droplet size of greater than or equal to 15 microns wherein the viscosity of the final emulsion is less than or equal to 1500 centipoise at 1 s⁻¹ and 80° F.
13. A method according to claim 12 wherein said phenol-formaldehyde ethoxylated resin is present in an amount of between 1 to 2%/wt. based on the total weight of the emulsifying additive.
14. A method according to claim 12 wherein said anionic surfactant is selected from the group consisting of carboxylic acids and sulphonic acids.
15. A method according to claim 14 wherein said anionic surfactant comprises ammonia dodecylbenzenesulphonate.
16. A method for the preparation of a low viscosity, nonaging hydrocarbon in water emulsion from a viscous hydrocarbon wherein aging of the emulsion over time is substantially eliminated comprising the steps of:
- (a) forming a concentrated emulsion by:
- (1) admixing said viscous hydrocarbon with an emulsifying additive comprising an alkyl phenol ethoxylated and a phenol-formaldehyde ethoxylated resin and water wherein a water content is less than or equal to 15%/wt.;
- (2) heating said mixture to a temperature of between about 120° F. to about 200° F.; and

- (3) stirring said heated mixture under controlled conditions so as to obtain a concentrated hydrocarbon in water emulsion having an average oil droplet size of less than or equal to 4 microns;
- (b) forming a final emulsion by:
- (1) diluting said concentrated hydrocarbon in water emulsion with water so as to obtain a water content greater than the water content of the concentrated emulsion and less than or equal to 30%/wt.;
- (2) heating said diluted mixture to a temperature of between about 140° F. to about 220° F.; and
- (3) stirring said heated mixture under controlled conditions so as to obtain a final hydrocarbon in water emulsion having an average oil droplet size of greater than or equal to 15 microns wherein the viscosity of the final emulsion is less than or equal to 1500 centipoise at 1 s⁻¹ and 80° F.
17. A method for the preparation of a low viscosity, nonaging hydrocarbon in water emulsion from a viscous hydrocarbon wherein aging of the emulsion over time is substantially eliminated comprising the steps of:
- (a) forming a concentrated emulsion by:
- (1) admixing said viscous hydrocarbon with an emulsifying additive comprising an ammonia dodecylbenzenesulphonate and a phenol-formaldehyde ethoxylated resin and water wherein a water content is less than or equal to 15%/wt.;
- (2) heating said mixture to a temperature of between about 120° F. to about 200° F.; and
- (3) stirring said heated mixture under controlled conditions so as to obtain a concentrated hydrocarbon in water emulsion having an average oil droplet size of less than or equal to 4 microns;
- (b) forming a final emulsion by:
- (1) diluting said concentrated hydrocarbon in water emulsion with water so as to obtain a water content greater than the water content of the concentrated emulsion and less than or equal to 30%/wt.;
- (2) heating said diluted mixture to a temperature of between about 140° F. to about 220° F. and
- (3) stirring said heated mixture under controlled conditions so as to obtain a final hydrocarbon in water emulsion having an average oil droplet size of greater than or equal to 15 microns wherein the viscosity of the final emulsion is less than or equal to 1500 centipoise at 1 s⁻¹ and 80° F.
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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,354,504

DATED : October 11, 1994

INVENTOR(S) : Hercilio Rivas et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In Column 8, claim 3, line 18, insert --1500--
before "rpm".

In Column 8, claim 4, line 21, "iS" should read
--is--.

In Column 8, claim 5, line 23, "methodi" should
read --method--.

In Column 8, claim 5, line 24, insert --3500--
before "to".

In Column 8, claim 6, line 29, "500 000" should
read --500,000--.

In Column 9, claim 12, line 18, "140 o F" should
read --140°F--.

In Column 9, claim 12, line 24, "1⁻¹" should
read --1 s⁻¹--.

Signed and Sealed this

Twenty-fifth Day of April, 1995

Attest:

Bruce Lehman

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks



US005480583A

United States Patent [19]
Rivas et al.

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[45] **Date of Patent:** **Jan. 2, 1996**

[54] **EMULSION OF VISCOUS HYDROCARBON
IN AQUEOUS BUFFER SOLUTION AND
METHOD FOR PREPARING SAME**

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[63] **Continuation-in-part of Ser. No. 801,472, Dec. 2, 19915,
419,852.**

[51] **Int. Cl.⁹** **B01J 13/00; C10L 1/32;
F17D 1/17**

[52] **U.S. Cl.** **252/311.5; 252/312; 44/301**

[58] **Field of Search** **252/312, 314,
252/8.551, 311.5, 311; 44/300, 301; 137/13;
507/232, 263, 264, 267**

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[57] **ABSTRACT**

A method for forming a stable emulsion of a viscous
hydrocarbon in an aqueous buffer solution includes the steps
of: providing a viscous hydrocarbon containing an inactive
natural surfactant and having a salt content by weight of less
than or equal to about 15 ppm and having a water content by
weight of less than or equal to about 0.1%; forming a
solution of a buffer additive in an aqueous solution to
provide a basic aqueous buffer solution, the buffer additive
being operative to extract and activate the inactive natural
surfactant from the viscous hydrocarbon; and mixing the
viscous hydrocarbon with the aqueous buffer solution at a
rate sufficient to provide an emulsion of the viscous hydro-
carbon in the aqueous buffer solution, whereby the buffer
additive extracts the inactive natural surfactant from the
viscous hydrocarbon into the aqueous buffer solution and
activates the inactive natural surfactant so as to stabilize the
emulsion. According to the invention, the buffer additive is
a water soluble amine. The inactive natural surfactant con-
tained in the viscous hydrocarbon includes carboxylic acids,
phenols, esters, and mixtures thereof. Bimodal emulsions,
having two distinct droplet size distributions, are also
formed according to the method of the present invention and
have improved viscosity characteristics.

1 Claim, No Drawings

EMULSION OF VISCOUS HYDROCARBON IN AQUEOUS BUFFER SOLUTION AND METHOD FOR PREPARING SAME

This application is a continuation-in-part of U.S. patent application Ser. No. 07/801,472, filed Dec. 2, 1991, now U.S. Pat. No. 5,419,852.

BACKGROUND OF THE INVENTION

The invention relates to an emulsion of a viscous hydrocarbon in an aqueous buffer solution for use as a combustible fuel.

Low gravity viscous hydrocarbons are found in large supply in Canada, Russia, the United States, China and Venezuela, and are normally liquids with viscosities ranging from 10,000 cp to more than 500,000 cp at ambient temperatures. These hydrocarbons are typically produced by numerous methods including steam injection, mechanical pumping, mining techniques and combinations of these methods.

Once produced, such hydrocarbons are useful as combustible fuel once they are desalted and dehydrated and have been treated to remove other undesirable constituents. As a liquid fuel, however, these hydrocarbons are too viscous for practical use. Thus, such viscous hydrocarbons are formed into hydrocarbon in water emulsions which have improved viscosity and, accordingly, improved flow characteristics. When formed with a high ratio of hydrocarbon material to water, these emulsions are an excellent combustible fuel. However, the emulsion is not stable and rapidly breaks if not stabilized with surfactants or emulsifiers. Unfortunately, commercial emulsifiers are expensive and the cost of the emulsion is therefore increased. This added cost obviously adversely impacts the viability of using viscous hydrocarbons to form combustible fuel emulsions.

Viscous hydrocarbons are known to naturally contain materials which are potential surfactants. It would of course be desirable to activate such materials so as to provide natural surfactants to stabilize the emulsion without the additional expense of commercial emulsifiers, thereby providing a more practical alternative for the use of viscous hydrocarbons in forming combustible fuel emulsions. The materials naturally contained in viscous hydrocarbons which are potential surfactants include numerous carboxylic acids, esters and phenols which, in basic pH environment, can be activated as natural surfactants. Sodium hydroxide has been used as an additive to provide the proper pH. However, sodium hydroxide is unable to keep the pH of the aqueous phase constant so that the proper pH, the activated surfactant and the emulsion itself are all short lived.

It is desirable, accordingly, to provide an emulsion stabilized with natural surfactants which does not require the addition of commercial surfactants and which emulsion resists aging and is useful as a combustible liquid fuel.

Accordingly, it is the principal object of the present invention to provide a combustible emulsion of a viscous hydrocarbon in water which emulsion utilizes the natural surfactants of the hydrocarbon to provide stability.

It is a further object of the invention to provide a method for forming such a combustible emulsion.

It is a still further object of the invention to provide such an emulsion and method whereby the emulsion formed is a bimodal emulsion having improved viscosity characteristics.

Other objects and advantages will appear hereinbelow.

SUMMARY OF THE INVENTION

The foregoing objects and advantages are attained by the disclosed emulsion and method for preparing same.

According to the invention, a stable emulsion of a viscous hydrocarbon in an aqueous buffer solution is formed by a method comprising the steps of providing a viscous hydrocarbon containing an inactive natural surfactant and having a salt content by weight of less than or equal to about 15 ppm and a water content by weight of less than or equal to about 01.%; forming a solution of a buffer additive in an aqueous solution to provide a basic aqueous buffer solution, the buffer additive being operative to extract and activate the inactive natural surfactant from the viscous hydrocarbon; and mixing the viscous hydrocarbon with the aqueous buffer solution at a rate sufficient to provide an emulsion of the viscous hydrocarbon in the aqueous buffer solution, whereby the buffer additive extracts the inactive natural surfactant from the viscous hydrocarbon into the aqueous buffer solution and activates the inactive natural surfactant so as to stabilize the emulsion.

According to the invention, the buffer additive is preferably a water soluble amine, and the inactive natural surfactant is selected from the group consisting of carboxylic acids, phenols, esters, and mixtures thereof.

According to a preferred embodiment of the invention, a bimodal emulsion is formed by a method wherein the mixing step includes a first mixing step wherein a first emulsion is prepared having a large droplet size D_L of between about 10 to about 40 μm , and a second mixing step wherein a second emulsion is prepared having a small droplet size D_S of less than or equal to about 5 μm , the method further including the step of mixing the first emulsion with the second emulsion so as to form a bimodal emulsion having a dispersed phase characterized by two droplet sizes corresponding to D_L and D_S .

DETAILED DESCRIPTION

The invention relates to an emulsion of a viscous hydrocarbon in an aqueous buffer solution which emulsion is useful as a combustible liquid fuel. The invention further relates to a method for preparing such a combustible emulsion without the use of commercial emulsifier or surfactant materials.

The present invention relates specifically to an emulsion and a method for forming an emulsion from a processed viscous hydrocarbon to provide a stable emulsion of the viscous hydrocarbon in an aqueous buffer solution without requiring commercial surfactants for stability. The emulsion so formed, referred to herein as the commercial emulsion sold by Intevep, S. A. under the trademark ORIMULSION™, is suitable for combustion as a liquid fuel and other end uses such as transportation to a refinery for further processing.

Naturally occurring viscous hydrocarbon materials are produced from deep wells through a number of mechanisms such as steam flooding, pumping, mining techniques and the like. Such natural viscous hydrocarbons are typically characterized, for example, by the following chemical and physical properties: C wt. % of 78.2 to 85.5; H wt. % of 9.0 to 10.8; O wt. % of 0.2 to 1.3; N wt. % of 0.50 to 0.70; S wt. % of 2.00 to 4.50; Ash wt. % of 0.05 to 0.33; Vanadium, ppm of 50 to 1000; Nickel, ppm of 10 to 500; Iron, ppm of 5 to 100; Sodium, ppm of 10 to 500; Gravity, °API of 0 to 16.0; Viscosity (cSt), 122° F. of 100 to 5,100,000; Viscosity

(cSt), 210° F. of 10 to 16,000; LHV (BTU/LB) of 15,000 to 19,000; and Asphaltene, wt. % of 5.0 to 25.0.

These naturally occurring viscous hydrocarbons are accompanied during production by formation water in at least small, and usually widely varying amounts. Although, as shown above, the hydrocarbon generally has a very high viscosity, primary emulsions formed downhole of the hydrocarbon in formation water can greatly reduce the viscosity so as to allow the hydrocarbon to be produced and transported to treatment stations, where the emulsion is typically degassed and desalted, and the primary emulsion is broken to separate away other undesirable constituents with the formation water. Such processing typically yields a viscous hydrocarbon having a salt content by weight of about 15 ppm or less, preferably about 10 ppm or less, and a water content by weight of about 0.1% or less, preferably 0%. The processed viscous hydrocarbon so obtained is the preferable starting material for forming the emulsion of the present invention and may, according to the present invention, be reconstituted without commercial emulsifiers into an emulsion such as the aforesaid ORIMULSION™ commercial product. U.S. Pat. No. 4,795,478, incorporated herein by reference, contains a detailed description of a method for processing naturally occurring viscous hydrocarbons to obtain processed viscous hydrocarbon suitable for forming ORIMULSION™, which processed viscous hydrocarbon is suitable starting material for the emulsion of the present invention. A treated Cerro Negro bitumen, for example, may suitably have the following physical and chemical properties:

CHARACTERISTICS OF TYPICAL TREATED CERRO NEGRO BITUMEN		
Water Content	(% w/w)	0.02
Carbon	(% p/p)	83.53
Hydrogen	(% p/p)	11.48
Ash	(% p/p)	0.102
Sulfur	(% p/p)	3.76
Total Nitrogen	(ppm)	8,376.00
Magnesium	(ppm)	21.92
Vanadium	(ppm)	599.0
Iron	(ppm)	8.71
Nickel	(ppm)	124.13
sodium	(ppm)	9.13
calcium	(ppm)	88.19
Conradson	(ppm)	15.18
Carbon		
Flash Point	(°F.)	246.00
Melting Point	(°F.)	75.00
Heating Power	(BTU/lb)	19,005.00
Raw		
Heating Power	(BTU/lb)	17,958.00
Net		

The desired processed viscous hydrocarbon starting material may suitably be obtained as follows. The viscous hydrocarbon material is produced downhole, for example, through diluent injection of kerosene so as to provide a hydrocarbon having an API gravity of about 14 with a viscosity low enough to allow the hydrocarbon to be pumped to the surface to treatment stations for conventional degassing, desalting and dehydration. The diluent is then removed, for example in a distillation tower, and a degassed, desalted and dehydrated viscous hydrocarbon results. This resulting degassed, desalted and dehydrated viscous hydrocarbon is then suitable for use in preparing commercial ORIMULSION™ products.

According to the invention, a combustible emulsion of the processed viscous hydrocarbon is formed in an aqueous buffer solution containing a buffer additive which extracts and activates natural surfactants from the viscous hydrocarbon so as to stabilize the emulsion without requiring commercial surfactants.

Most naturally occurring viscous hydrocarbon material contains inactive surfactants including carboxylic acids, phenols and esters which, under proper conditions, can be activated as surfactants. It is known, for example, that these surfactants can be activated for a short time with NaOH. NaOH provides a basic solution in which the inactive natural surfactants can be activated, but emulsions so formed are not stable because the NaOH is rapidly depleted by other constituents in the hydrocarbon.

According to the invention, a buffer additive is used which provides a much broader and longer lasting window during which the solution containing the additive has a basic pH, preferably between about 11 to about 13, and therefore yields a more stable emulsion. The buffer additive serves to raise and buffer the pH of the continuous aqueous phase of the emulsion. The buffer additive extracts and activates the natural surfactants from the viscous hydrocarbon, into the aqueous buffer solution, thus stabilizing the viscous hydrocarbon-in-aqueous buffer solution emulsion without the use of costly commercial surfactants or emulsifiers.

According to the invention, the buffer additive is a water soluble amine. Amines are nitrogen compounds which may be derived from ammonia by replacing one or more hydrogens with an alkyl group. Amines having a single alkyl group such as, for example, isopropylamine, are suitable for providing stable emulsions. Amines with two or more alkyl groups, however, require the presence of a small amount of an alkali metal, or an alkaline earth metal, referred to herein as an alkali additive, preferably in the form of an alkali metal salt or an alkaline earth metal salt, to activate the inactive natural surfactants of the hydrocarbon. Such multiple group amines include, for example, ethylamine, diethylamine, triethylamine, propylamine, sec-propylamine, dipropylamine, butylamine, sec-butylamine, tetramethylethylammonium hydroxide, tetrapropylammonium hydroxide, and mixtures thereof.

Suitable alkali additive may include any alkali metal or alkaline earth metal, and may preferably include sodium, calcium and/or magnesium, which may be added in any form, preferably in the form of a salt, such as, for example, sodium chloride, potassium chloride, sodium nitrate, potassium nitrate, calcium nitrate, magnesium nitrate, and mixtures thereof. Such salts are preferable because they are, for the most part, readily and affordably available.

The combustible emulsion is formed by mixing the processed viscous hydrocarbon with an aqueous solution of the buffer additive with sufficient mixing energy to emulsify the mixture and provide an emulsion of the viscous hydrocarbon discontinuous phase in the aqueous buffer solution continuous phase having desired droplet size and viscosity.

The aqueous buffer solution is a solution of the buffer additive in water. The buffer additive is preferably added in a concentration in the aqueous buffer solution of at least about 500 ppm in order to provide a basic aqueous buffer solution, preferably having a pH of between about 11 to about 13. Concentrations of greater than 15,000 ppm are not preferred because no apparent benefit is obtained for the additional cost of adding such additional concentrations of buffer additive. More preferably, buffer additive is added at a concentration of between about 500 ppm to about 10,000 ppm.

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When necessary, the alkali additive is added at a concentration of between about 50 ppm to about 500 ppm, preferably between about 50 ppm to about 100 ppm.

When the viscous hydrocarbon and aqueous solution are mixed, the natural surfactants are extracted from the viscous hydrocarbon into the aqueous buffer solution and activated by the buffer additive to provide natural and active surfactants in the aqueous buffer solution continuous phase of the emulsion. The aqueous buffer solution has a buffered pH preferably in the range of about 11 to about 13, more preferably between about 11.3 to about 11.8. The basic pH of the aqueous buffer solution is provided by the buffer additive and is critical in providing a stable emulsion. The buffering of the pH serves to prevent a breaking of the emulsion due to changes in pH which may be caused by pumping, handling, pressure and temperature surges and mixing. Further, the buffer additive of the present invention provides the desired pH of the aqueous buffer solution over a broad range of concentration of the buffer additive in the aqueous buffer solution. Thus, changes in the concentration of the buffer additive, which are to be expected over time, do not result in an aging and breaking of the emulsion.

The mixing step is carried out so as to supply sufficient energy to the mixture to yield an emulsion having the desired physical characteristics of the ORIMULSION™ end product, especially droplet size and viscosity. In general, smaller droplet sizes require more mixing energy, larger concentration of emulsifier (natural surfactant and buffer additive) or both. According to the invention, the emulsion is mixed with sufficient mixing energy to yield an average droplet size of 30 μm or less. Such an emulsion will have a viscosity below about 1500 cp at 30° C. and 1 sec^{-1} . A conventional mixer, for example, may suitably mix the emulsion at a rate of at least about 500 rpm. The reduced viscosity of the emulsion so formed allows the use of the viscous hydrocarbon as a source of useful combustible fuel and is obtained without the added cost of commercial surfactants.

The ratio of hydrocarbon phase to aqueous phase has been found to effect the viscosity of the emulsion. In addition, a high ratio of hydrocarbon phase to aqueous phase is desirable so as to provide a combustible emulsion suitable for atomizing and combustion as a fuel without further treatment. Thus, the ratio of hydrocarbon to aqueous buffer solution, by weight, is preferably at least 50:50 and more preferably is between about 75:25 to about 95:5. Naturally, formation of emulsions having high ratios of hydrocarbon to aqueous buffer solution will require larger concentrations of the buffer additive within the specified range.

According to a preferred embodiment of the invention, the combustible emulsion is prepared so as to provide two distinct droplet populations in the dispersed phase of the emulsion. Such an emulsion, called a bimodal emulsion, has still further improved viscosity characteristics and is prepared according to the invention without commercial surfactants.

According to the invention, a bimodal emulsion can be formed by preparing an aqueous solution of the buffer additive and providing a viscous hydrocarbon as above. Two emulsions are then formed, each having a different droplet size. The first emulsion has a large average droplet size, D_L , which is preferably between about 10 μm to about 40 μm , and more preferably between about 15 μm to about 30 μm . The second emulsion is formed with a small average droplet size, D_S , which is preferably less than or equal to about 5 μm , and more preferably less than or equal to about 2 μm .

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The two emulsions are then mixed so as to form a stable bimodal emulsion, as described above, with two distinct droplet sizes, D_L and D_S , in the dispersed phase.

It has been found that the viscosity of the bimodal emulsion is controlled by the ratio of the weight of large droplet size emulsion to the weight of small droplet size emulsion, as well as by the ratio of the average droplet size D_L of the large droplet size emulsion to the average droplet size D_S of the small droplet size emulsion.

Preferably, between about 70% to about 80% by weight of the dispersed hydrocarbon phase will be in the large droplet size emulsion, and the ratio of D_L to D_S is at least about 4 and more preferably is at least about 10. These values can be manipulated during preparation of the emulsion by altering the mixing energy used to form one or both emulsions so as to control the resulting droplet size, and also by selecting the appropriate volumes of each emulsion to be mixed.

Emulsions formed according to the invention exhibit low viscosity and good stability which greatly facilitates the use of viscous hydrocarbons as the source of combustible liquid fuel. Further, the emulsions are formed without using costly commercial emulsifiers.

The preparation of emulsions according to the invention will be further illustrated in the following examples.

EXAMPLE 1

A number of emulsions were prepared using HIPR techniques as disclosed in U.S. Pat. No. 4,934,398. A Cerro Negro natural bitumen from the Cerro Negro Oil Field in Venezuela was degassed, dehydrated and desalted to provide a starting processed viscous hydrocarbon.

The emulsions were prepared in an aqueous buffer solution containing, as a buffer additive, a water soluble amine additive marketed under the trademark INTAMINE™ by Intevep, S. A.

Emulsions were prepared having ratios, by weight, of hydrocarbon to aqueous buffer solution of 94:6, 90:10, 85:15, and 80:20, using buffer additive concentrations of between 500 ppm to 10,000 ppm.

The mixing step was carried out at 60° C. for mixing times which were controlled to yield emulsions having average droplet sizes of 2, 4, 20 and 30 μm .

These emulsions were then diluted to yield hydrocarbon/ aqueous phase ratios of 70:30, 75:25, and 80:20.

All emulsions were stabilized without the use of commercial surfactants, even those having droplet sizes of less than 3 μm .

EXAMPLE 2

Emulsions were prepared using a single group buffer additive, isopropylamine, at concentrations of 6000 ppm and 7000 ppm. The emulsions were mixed at a hydrocarbon/ aqueous phase ratio of 94:6, at 500 rpm. Table I below summarizes the average droplet sizes obtained at mixing times of between 0.5 to 5.0 minutes.

TABLE I

Mixing time (min)	DROPLET SIZE DIAMETER (microns)	
	Buffer Concentration (ppm)	
	6000	7000
0.5	7.4	3.7
1	2.4	1.5

TABLE 1-continued

Mixing time (min)	DROPLET SIZE DIAMETER (microns) Buffer Concentration (ppm)	
	6000	7000
2	1.5	1.3
4	1.4	1.2
5	1.3	1.2

As can be seen, droplet sizes well below 3 μ m were obtained without the use of commercial surfactants.

EXAMPLE 3

Emulsions were prepared using several concentrations of isopropylamine as a buffer additive. Emulsions were prepared under mixing at 500 rpm for 2 minutes having a ratio of hydrocarbon to aqueous phase of 80:20 and having average droplet size and viscosity as shown below in Table 2.

TABLE 2

Buffer Concentration (ppm)	Droplet Size Diameter (microns)	Viscosity (20/Sec) (cp)
3000	18.45	800
5000	16.74	1145
7000	12.34	1285

EXAMPLE 4

Emulsions were prepared using a two group amine (diethylamine) at a concentration of 3000 ppm. An alkali salt, NaCl, was also added to the aqueous solution at a concentration of 50 ppm. Emulsions having hydrocarbon/ aqueous phase ratios of 90:10, 85:15 and 80:20 were formed at 500 rpm having droplet sizes as shown below in Table 3.

TABLE 3

Mixing Time (Min)	RATIO: BITUMEN/AQUEOUS BUFFER SOLUTION		
	90/10 Average Droplet Size Diameter (Microns)	85/15	80/20
0.5	16.15	27.74	27.70
1	15.90	27.59	27.13
2	14.63	24.69	21.33
4	13.89	21.62	22.19
10	11.00	15.86	18.41

EXAMPLE 5

Emulsions were prepared at a mixing rate of 500 rpm using concentrations of 5000 ppm of diethylamine and 50 ppm NaCl. Table 4 shows the average droplet size obtained for these emulsions.

TABLE 4

Mixing Time (Min)	RATIO: BITUMEN/AQUEOUS BUFFER SOLUTION			
	94/6 Average Droplet Size Diameter (Microns)	90/10	85/15	80/20
0.5	7.36	9.69	11.84	23.50
1	6.85	9.23	11.70	21.44
2	6.16	8.87	11.08	20.55
4	5.02	8.37	10.49	18.99
10	3.74	6.67	9.05	15.68

EXAMPLE 6

Emulsions were prepared at a mixing rate of 500 rpm using concentrations of 7000 ppm of diethylamine and 50 ppm NaCl. Table 5 shows the average droplet size obtained.

TABLE 4

Mixing Time (Min)	RATIO: BITUMEN/AQUEOUS BUFFER SOLUTION			
	94/6 Average Droplet Size Diameter (Microns)	90/10	85/15	80/20
0.5	5.72	7.13	10.08	17.13
1	5.14	6.87	9.85	16.19
2	4.63	7.63	9.34	14.22
4	3.96	6.35	8.78	13.68
10	2.05	5.59	7.70	11.46

As shown, at concentrations of 7000 ppm, diethylamine yields emulsions having droplet size less than 3 μ m without using commercial emulsifiers.

The following Examples 7-11 illustrate preparation of bimodal emulsions, according to the invention, without the use of commercial emulsifiers.

EXAMPLE 7

Emulsions were prepared using HPR techniques as shown in U.S. Pat. No. 4,934,398 and using Cerro Negro natural bitumen from the Cerro Negro Oil Field in Venezuela. The emulsions were made as shown in Table 6 using an aqueous buffer solution of a water soluble amine, marketed under the trademark INTAMINE™, by Intevep, S. A., at concentrations of between 500 ppm and 10,000 ppm. The mixture was heated to 60° C. and stirred, changing the mixing speed and mixing time so as to obtain emulsions having average droplet sizes as indicated below in Table 6.

All emulsions were stabilized without the use of commercial surfactants or emulsifiers.

TABLE 6

EMULSION	BITUMEN/WATER (by weight)	DROPLET DIAMETER MICRONS	VISCOSITY (cp) AT 1 sec ⁻¹ AND 30° C.
1	70/30	2.1	16,000
2	70/30	4.3	11,000
3	70/30	20.7	3,000
4	70/30	29.8	2,500
5	75/25	2.1	52,000
6	75/25	4.3	30,000
7	75/25	20.7	9,500
8	75/25	29.8	6,000
9	80/20	2.1	100,000
10	80/20	4.3	38,000
11	80/20	20.7	17,000
12	80/20	29.8	8,500

Emulsions 2 and 3, those having a hydrocarbon:water ratio of 70:30 and average droplet size distributions, respectively, of 4.3 and 20.7 microns, were mixed together in different proportions and the viscosities of the resultant bimodal emulsions were measured. The results are shown in Table 7 below.

Table 8 shows the relationship between viscosity of a bimodal emulsion and the effect of the ratio of large mean droplet size to small mean droplet size (D_L/D_S) for emulsions with a ratio of hydrocarbon:water of 70:30% by weight. It can be seen that the bimodal emulsion viscosity increases when there is an increase in the fraction having

TABLE 7

EMULSION	% BY WEIGHT EMULSION W/MEAN DROPLET SIZE OF 4.3 MICRONS	% BY WEIGHT EMULSION W/MEAN DROPLET SIZE OF 20.7 MICRONS	VISCOSITY (cp) AT 1 sec ⁻¹ AND 30° C.
A	100	0	11,000
B	75	25	5,000
C	50	50	400
D	25	75	90
E	0	100	3,000

Table 7 shows that a relationship exists between the viscosity of the emulsion and the fraction of the hydrocarbon phase in the large droplet size emulsion (20.7 microns) and small droplet size emulsion (4.3 microns). In order to obtain the lowest viscosity value both droplet fractions must be clearly defined as two identifiable and distinct droplet sizes. Optimum viscosity is obtained at a ratio of large droplet size emulsion to small droplet size emulsion of about 75:25 by weight.

small mean diameter droplet size. However, all the viscosity values reported for emulsions F, G and H are far below the viscosity of monomodal emulsions having 70% by weight hydrocarbon as the dispersed phase. (See Table 6)

EXAMPLE 8

Bimodal emulsions containing 75% by weight of a large droplet size emulsion D_L and 25% by weight of a small droplet size emulsion D_S in a total hydrocarbon to water ratio in the final emulsion product of 70:30 were made from the emulsions of Table 6 as shown in Table 8 below.

EXAMPLE 9

With Emulsions as prepared in Example 7 and having characteristics as shown in Table 6, bimodal emulsions containing 75% by weight of a large droplet size emulsion D_L and 25% by weight of a small droplet size emulsion D_S in a total hydrocarbon to water ratio in the final emulsion product of 75:25 were produced as shown in Table 9.

TABLE 8

EMULSION	MEAN DROPLET SIZE		RATIO: DROPLET SIZE D_L/D_S	RATIO BY WT. OF EMUL. D_L / EMUL. D_S	VISCOSITY (cp) AT 1 sec ⁻¹ AND 30° C.
	D_S MICRONS	D_L MICRONS			
F	2.1	29.8	14	75/25	66
G	4.3	29.8	7	75/25	90
H	4.3	20.7	4.8	75/25	128

TABLE 9

EMULSION	MEAN DROPLET SIZE		RATIO: DROPLET SIZE D_L/D_S	RATIO BY WT. OF EMUL. D_L / EMUL. D_S	VISCOSITY (cp) AT 1 sec ⁻¹ AND 30° C.
	D_S MICRONS	D_L MICRONS			
I	2.1	20.7	10	75/25	180
J	4.3	20.7	4.8	75/25	600
K	2.1	29.8	14	75/25	150
L	4.3	29.8	6.9	75/25	300

Table 9 shows the relationship between viscosity and the ratio of large mean droplet size to small mean droplet size (D_L/D_S) for bimodal emulsions with an hydrocarbon to water ratio of 75:25 by weight.

It can be seen that a viscosity below 1500 cp at 1 sec⁻¹ and 30° C. can be obtained when the ratio of large mean droplet size to small mean droplet size (D_L/D_S) is greater than or equal to 4.

EXAMPLE 11

With the emulsions prepared in Example 7 and having characteristics as shown in Table 6, further bimodal emulsions were prepared having different ratios by weight of emulsion having large mean droplet size D_L to emulsion having small mean droplet size D_S as shown in Table 11.

EXAMPLE 10

With emulsions as prepared in Example 7 and having characteristics as shown in Table 6, further bimodal emulsions having different ratios of (D_L/D_S) and containing 75% by weight of a large droplet size emulsion D_L and 25% by weight of a small droplet size emulsion D_S in a total hydrocarbon to water ratio in the final emulsion product of 80:20 were prepared as shown in Table 10.

TABLE 10

EMULSION	MEAN DROPLET SIZE		RATIO: DROPLET SIZE D_L/D_S	RATIO BY WT. OF EMUL. D_L / EMUL. D_S	VISCOSITY (cp) AT 1 sec ⁻¹ AND 30° C.
	D_S MICRONS	D_L MICRONS			
M	2.1	20.7	10	75/25	1,100
N	4.3	20.7	4.8	75/25	14,000
O	2.1	29.9	14	75/25	450
P	4.3	29.8	7	75/25	7,500

Table 10 shows the relationship between viscosity and the ratio of large mean droplet size to small mean droplet size (D_L/D_S) for bimodal emulsions with a hydrocarbon:water ratio of 80:20 by weight. It can be seen that with a bimodal emulsion having a ratio of hydrocarbon:water of 80:20, in other words 80% dispersed hydrocarbon phase, it is neces-

TABLE 11

EMULSION	MEAN DROPLET SIZE		RATIO: DROPLET SIZE D_L/D_S	RATIO BY WT. OF EMUL. D_L / EMUL. D_S	VISCOSITY (cp) AT 1 sec ⁻¹ AND 30° C.
	D_S MICRONS	D_L MICRONS			
Q	2.1	29.8	14	80/20	600
R	2.1	29.8	14	75/25	450
S	2.1	29.8	14	70/30	800
T	2.1	29.8	14	65/35	1,500

sary that the ratio of large mean droplet size to small mean droplet size (D_L/D_S) should be greater than or equal to about 10 in order to obtain a viscosity below 1500 cp at 1 sec⁻¹ and 30° C.

Table 11 shows the relationship between viscosity and proportion by weight of small mean droplet size to large mean droplet size (D_L/D_S) for bimodal emulsions with an hydrocarbon to water ratio of 80:20 by weight. It can be seen that the viscosity of a bimodal emulsion having a ratio of hydrocarbon:water of 80:20 can be modified by changing the proportion of hydrocarbon by weight in the small mean droplet and large mean droplet size emulsions. When the amount of hydrocarbon in the emulsion having small mean droplet size is increased, the viscosity first decreases and then increases.

Thus, according to the invention, combustible emulsions are prepared from viscous hydrocarbons and stabilized without the use of commercial surfactants. The emulsions so prepared exhibit excellent viscosity characteristics which are even further improved by formulating bimodal emulsions. The provision of low viscosity combustible emulsion without the added cost of commercial surfactants, provides an excellent use of viscous hydrocarbons as a source of combustible material.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be

embraced therein.

What is claimed is:

1. A viscous hydrocarbon-in-aqueous buffer solution emulsion, comprising:

a viscous hydrocarbon discontinuous phase having a salt content by weight of less than or equal to about 15 ppm and having a water content of less than or equal to about 0.1%, said discontinuous oil phase comprises a viscous hydrocarbon having an API gravity of ≤ 15 and a viscosity at 1 sec^{-1} and 30°C. of $>5000 \text{ cps}$ and being characterized by two distinct oil droplet sizes D_L and D_S wherein D_L is about $10\text{--}40 \mu\text{m}$ and D_S is $\leq 5 \mu\text{m}$, the ratio of D_L/D_S is $\geq$ about 4 and about 72–80% by wt. of the viscous hydrocarbon has a large droplet size D_L ; and

a basic aqueous buffer solution continuous phase containing a buffer additive and a natural surfactant, the natural surfactant being an inactive surfactant naturally contained in the viscous hydrocarbon which inactive surfactant is extracted and activated by the buffer additive so as to stabilize the viscous hydrocarbon-in-aqueous buffer solution emulsion wherein the inactive natural surfactant is selected from the group consisting of carboxylic acids, phenols, esters and mixtures thereof.

* * * * *

(No Model.)

I. WANTLING & J. T. JOHNSON.
COAL CUTTING MACHINE.

No. 475,833.

Patented May 31, 1892.

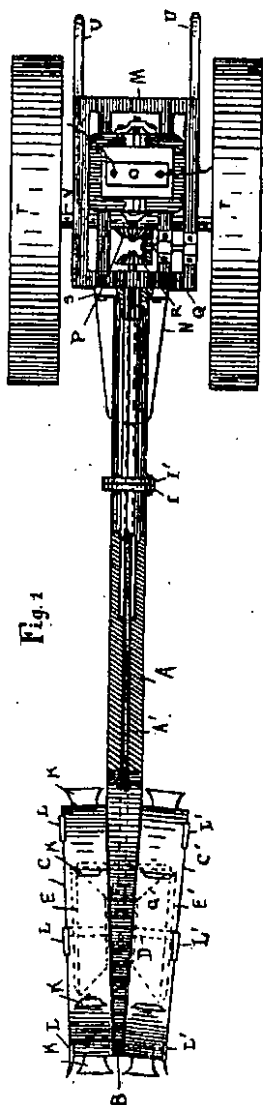


Fig. 1

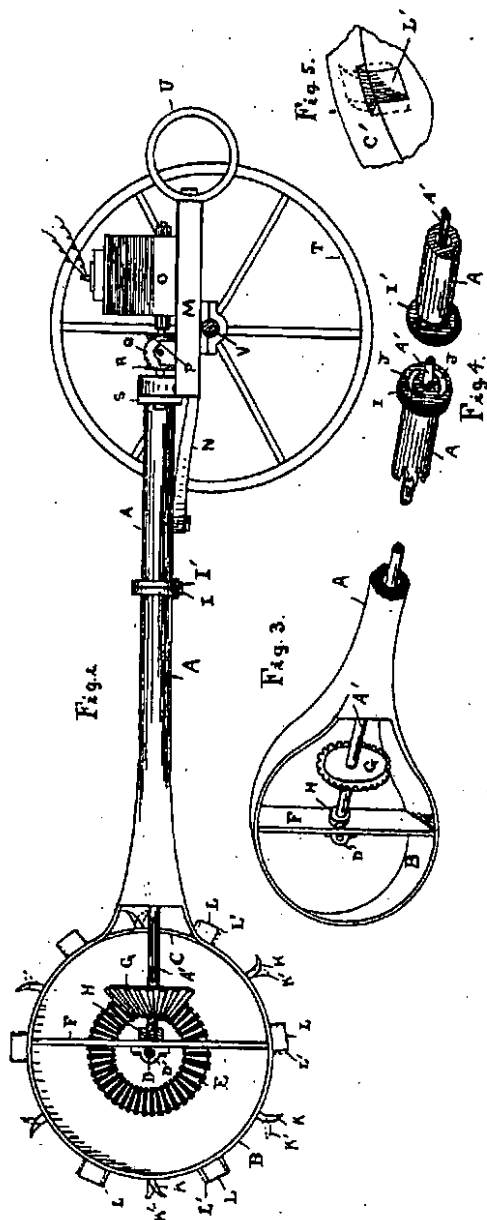


Fig. 2

Fig. 3

Fig. 4

Fig. 5

Witnesses.
R. N. McCormick
G. Keithley

Inventor
Isaac Wantling
James T. Johnson
By Wm. H. Abbott

THE MORRIS PETERS CO. PHOTO-LITHO, WASHINGTON, D. C.

UNITED STATES PATENT OFFICE.

ISAAC WANTLING AND JAMES T. JOHNSON, OF PEORIA, ILLINOIS.

COAL-CUTTING MACHINE.

SPECIFICATION forming part of Letters Patent No. 475,933, dated May 31, 1892.

Application filed November 26, 1891. Serial No. 413,113. (No model.)

To all whom it may concern:

Be it known that we, ISAAC WANTLING and JAMES T. JOHNSON, citizens of the United States, residing at Peoria, in the county of Peoria and State of Illinois, have invented certain new and useful Improvements in Coal-Cutting Machines; and we do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

Our invention relates to certain new and useful improvements in coal-cutting machines, by means of which a machine is provided being simple in construction, durable, and effective in operation, for the purposes designed.

More particularly our invention relates to that class of cutting-machines provided with rotary cutting-wheels having cutting-tools adjusted thereon, the said wheels being designed to be rotated very rapidly.

Our invention consists, essentially, of the adjustment and formation of two wheels adapted to be rotated in opposite directions, and provided with suitable gear formation within the said wheels, and suitable gear connection for operating the said wheels in opposite directions, and with the said wheels provided with suitable cutting-tools, all of which matters of form and detail structure will be explained more fully hereinafter.

That our invention may be more fully understood, reference is had to the accompanying drawings, in which—

Figure 1 is a plan view of our invention, showing the same connected with a mounted power. Fig. 2 is a side view thereof in section, showing the same mounted connection with the power for operation of the same. Fig. 3 is a detailed view of a frame structure designed to be carried between the wheels. Fig. 4 is a detailed view showing the manner of connection between sections of tubing or pipe. Fig. 5 is a detailed view showing the adjustment of a cutting-tool within the periphery of the wheels in the figures.

A is a tube cored out to provide for the carrying of the shaft A', the said tube A being formed at its forward end into the loop

or frame-work B, as shown in Fig. 3, provided at its central portion with the perpendicular frame-piece F, and upon the central portion of the frame-piece F is adjusted the clamp or box D', purposed to carry the axle D, the said axle being secured firmly within the box so as to be rigid that it may not turn.

C C' are wheels journaled upon the axle D, the axles being so turned as to provide for the adjustment of the wheels C C' obliquely with reference to the tube A and at an angle with each other, the frame-work or periphery B being formed to completely fill the space between the said wheels and to conform with and be in perfect alignment with the peripheries of the said wheels. The wheels C C' are provided with the internal spur gear-wheels E E', the same being cut from out the solid wheel, therefore being integral therewith and with the apex of the respective miter gear-wheels, bearing inward to the inner edges of the respective wheels C C'.

K K K K are cutting-tools set in or fixed upon the surfaces of the respective wheels C C' and formed to bear forward in the direction of rotation of the respective wheels, they therefore being adjusted at opposites with one another—that is, upon the different wheels.

L L L' L' L', &c., are cutting-tools set in the outer faces of the wheels C C' and designed to be curved outward and bear slightly above the cutting-tools K K, &c., for the purpose of cutting and trimming the surfaces of the body being cut. The shaft A', journaled within the tube A, bearing forward, is secured at its extreme forward end in the socket H by means of a small pin being carried through and bearing within a groove cut in the circumference of the said shaft at its forward extremity, thus enabling it to turn freely within the said socket H, but preventing it from being withdrawn therefrom by means of the pin and groove. Upon the shaft A' is carried the miter gear-wheel G and adjusted as to mesh with the respective miter gear-wheels E E', and is keyed securely upon the shaft in such position.

The tube A is made in section connected by means of the rims I I', being bolted to-

gether to accommodate the adjustment of the cutting-wheels in a vertical or horizontal position, as desired, and to facilitate this adjustment the slots J J are provided in the rim I, through which the bolts bear, which provides for a ready turning of the tube without a complete detachment of the bolts; but the sections may be clamped or secured in any suitable manner, and any expedient may be adopted to facilitate adjustment at the extremity of the tube A. There is shown in the drawings a connection with a carriage upon which is mounted a motor designed to show the application of power to provide for the operation of the device.

The carriage consists, essentially, of the frame-work M, mounted upon the wheels T T and provided with the forward brace N and also the hand-holds U, V being the axle provided for the wheel. O represents the motor bearing upon its shaft the spur-wheel P, which meshes with the intermediate spur-wheel Q, which in turn meshes with the spur-wheel R, the same being keyed upon the shaft A', thus completing the connection between the device and the operating means, it being supposed, of course, that the motor has the proper connection with the dynamo, that has sufficient capacity to operate the machine.

The cutting-wheels are adjusted obliquely with the shaft to provide width at base of cutting-head thus formed for insertion of pinion G, and narrows at the forward part to bring the cutting-tools nearer together to cut out the middle. The cutting-tools L L' are provided and bent outward from the faces of the cutting-wheels, so that as the cutting-head bears forward in the body of coal they will clear the sides, cutting it away gradually as it moves forward.

In operation as in coal-mining, the adjustment of the various parts being made as herein shown or in such other adjustments as to bear out the principle herein involved, power being applied through and by means of a motor, an engine, or any power desired to be used. The shaft A' is caused to be rotated, in which rotation a corresponding rotary motion is conveyed to the miter gear-wheel G. The same, meshing with the miter gear-wheels E E', conveys a rotary motion to the said miter gear-wheels and to the wheels C C', said wheels rotating in opposite direction and being rapidly rotated and being provided with the cutting-tools, as shown, and borne forward against a body designed to be penetrated—as, for instance, a body of coal—the coal will be quickly cut away, and it can be run into the body of coal a considerable distance. In the adjustment here shown a perpendicular cut will be made, it being designed to be borne forward by pressure, which may be applied from the hand-holds U U, and the frame-work is so adjusted upon the axle

V that the machine may be tilted upward or downward, as desired, it being designed in operation that a long perpendicular cut be made by the playing up and down within a long cut, thus cutting it out gradually. A horizontal cut may be made by merely adjusting the cutting device or the wheels at right angles with the position here shown, the operation and mode of applying power being identical with that herein shown.

The advantages possessed by the use of this device are numerous. Chief among them is its simple adaptation for the purpose designed and the adaptability of the device to accommodate itself to any degree or kind of power that may be desired to be used. In the operation of coal-mining the opposite rotation of the wheels equalizes the draft and reduces it to the minimum, thus gaining a great advantage over cutting-wheels rotated in the same direction, which are always accompanied with an immense draft, which hinders greatly the successful operation of such machines.

The various parts of the device herein shown may be varied in form or adjustment to suit the application in which they may be desired to be used, retaining always the principle herein involved.

Having thus fully described our invention, what we claim, and desire to secure by Letters Patent, is—

1. The combination, in a coal-mining machine, of the cutting-wheels C C', provided with the cutting-tools K K, L L, L' L', &c., upon their outer surfaces and with the internal miter gear-wheels E E' and journaled upon the axle D, with the miter gear-wheel G, meshing with the miter gear-wheels E E' and carried upon the shaft A', the frame-work B, provided with the perpendicular frame-piece F, which supports the axle D by means of the box D' and the end of the shaft A' by means of the socket H, the tube A, which incloses and provides a journal-bearing for the shaft A', and the rims I I', which unite the sections of the two, all connected with any suitable power, all substantially as described and set forth.

2. The combination, in a coal-cutting machine, of the obliquely-adjusted cutting-wheels C C', provided with the cutting-tools K L and the internal gear or cogs E E', with the frame-work B, having the extension-tube A integral therewith, and the shaft A', journaled in the cross-piece F of the frame-work B and in the tube A, and having keyed thereon the pinion-wheel G, adjusted to mesh with the gear-cogs E E' on the cutting-wheels C C' to rotate them in opposite directions, all substantially as described and set forth.

3. In a coal-cutting machine, the combination, with the shaft D, carried in the cross-piece F and angled at its extremities, of the cutting-wheels C C' to give the wedge shape

to the cutting-head by the wheels being carried upon the angles of the shaft, the pinion G, carried upon the shaft A' and meshing with the cogs of the gear E E' to rotate the
5 wheels in opposite directions, and the framework B, provided with the tube-extension A, all substantially as described and set forth.

In testimony whereof we affix our signatures in presence of two witnesses.

ISAAC WANTLING.
JAMES T. JOHNSON.

Witnesses:

JOSIE TEEFT,
R. N. MCCORMICK.

Correction in Letters Patent No. 475,833.

It is hereby certified that in Letters Patent No. 475,833, granted May 31, 1892, upon the application of Isaac Wantling and James T. Johnson, of Peoria, Illinois, for an improvement in "Coal-Cutting Machines," an error appears in the printed specification requiring correction, as follows: In lines 1-2, page 3, the words "work B, provided with the tube extension A, all substantially as described and set forth," should be stricken out and inserted after line 7 as now numbered, same page; and that the Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed, countersigned, and sealed this 14th day of June, A. D. 1892.

[SEAL.]

CYRUS BUSSEY,

Assistant Secretary of the Interior.

Countersigned:

W. E. SIMONDS,

Commissioner of Patents.



US005641433A

United States Patent [19]
Chirinos et al.

[11] **Patent Number:** 5,641,433
[45] **Date of Patent:** Jun. 24, 1997

[54] **PREPARATION OF HIPR EMULSIONS**

[75] **Inventors:** Maria Luisa Chirinos, Caracas, Venezuela; Alistair Stewart Taylor, Yateley; Spencer Edwin Taylor, Camberley, both of United Kingdom

[73] **Assignee:** Intevep, S.A., Caracas, Venezuela

[21] **Appl. No.:** 476,495

[22] **Filed:** Jun. 7, 1995

Related U.S. Application Data

[63] Continuation of Ser. No. 44,913, Apr. 8, 1993, abandoned, which is a continuation of Ser. No. 500,135, Mar. 28, 1990, abandoned, and a division of Ser. No. 201,271, Jun. 2, 1988, Pat. No. 4,934,398, which is a continuation of Ser. No. 919,601, Oct. 14, 1986, abandoned, which is a continuation of Ser. No. 700,814, Jan. 25, 1985, abandoned.

[51] **Int. Cl.⁶** B01J 13/00; F17D 1/16

[52] **U.S. Cl.** 252/312; 137/13; 252/314

[58] **Field of Search** 252/312, 314; 44/301; 137/13

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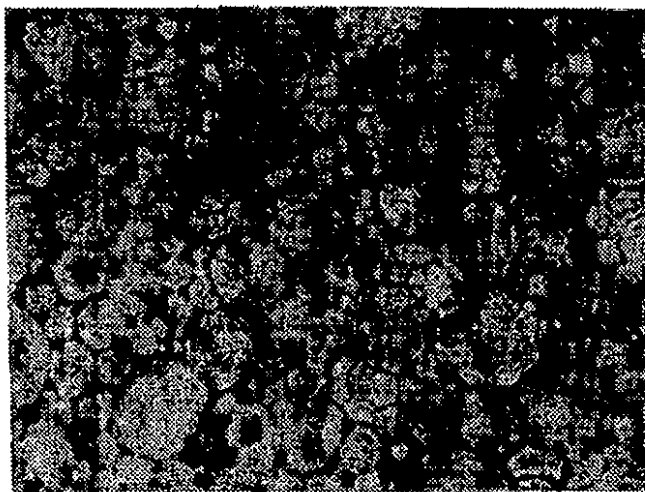
Primary Examiner—Richard D. Lovering
Attorney, Agent, or Firm—Bachman & LaPointe, P.C.

[57] **ABSTRACT**

An HIPR (high internal phase ratio) emulsion of oil in water is prepared by directly mixing 70 to 98% by volume of a viscous oil having a viscosity in the range 200 to 250,000 mPa.s at the mixing temperature with 30 to 2% by volume of an aqueous solution of an emulsifying surfactant or an alkali, percentages being expressed as percentages by volume of the total mixture. Mixing is effected under low shear conditions in the range 10 to 1,000 reciprocal seconds in such manner that an emulsion is formed comprising highly distorted oil droplets having mean droplet diameters in the range 2 to 50 micron separated by thin interfacial films. The emulsions are much less viscous than the oils from which they are prepared and may, optionally after dilution, be pumped through a pipeline.

11 Claims, 4 Drawing Sheets

FIG. 1



10 μ m

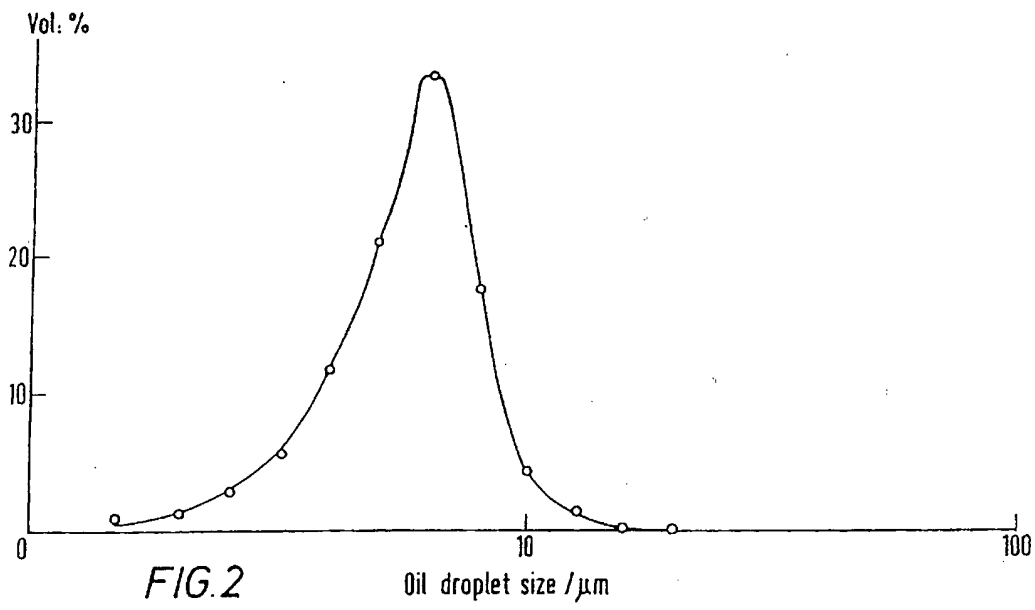
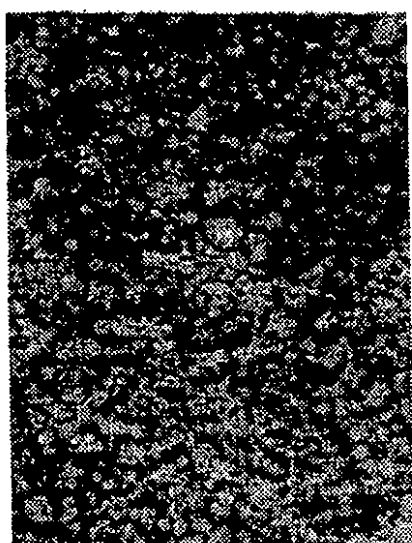


FIG. 2

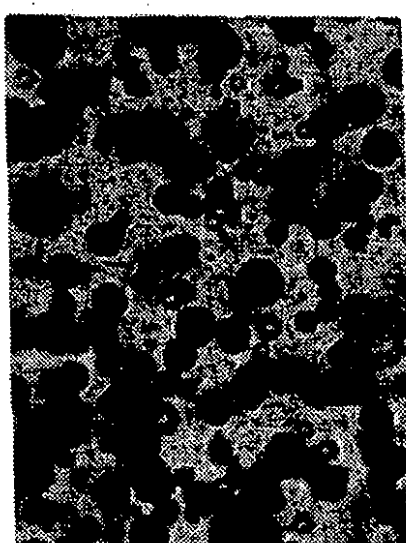
FIG. 3A-1



90 per cent HIPIR o/w emulsion

25 μ m

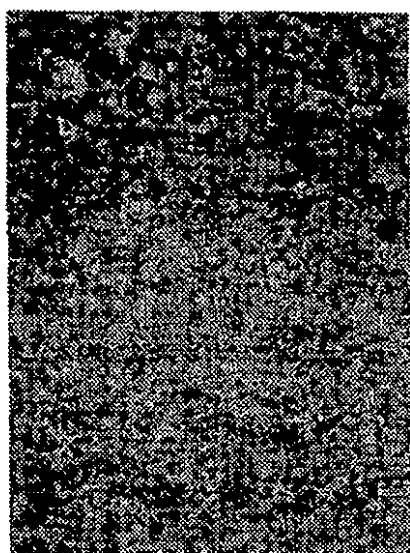
FIG. 3A-2



Diluted emulsion

25 μ m

FIG. 3B-1



90 per cent HIPIR o/w emulsion

25 μ m

FIG. 3B-2



Diluted emulsion

25 μ m

PREPARATION OF HIPR EMULSIONS

RELATED APPLICATIONS

The instant application is a continuation of U.S. patent application Ser. No. 08/044,913 filed Apr. 8, 1993 and now abandoned, which application is a continuation of U.S. patent application Ser. No. 07/500,135 filed Mar. 28, 1990 and now abandoned, and a division of U.S. patent application Ser. No. 07/201,271 filed Jun. 2, 1988, now U.S. Pat. No. 4,934,398, which is a continuation of U.S. patent application Ser. No. 06/919,601 filed Oct. 14, 1986 and now abandoned, which is a continuation of U.S. patent application Ser. No. 06/700,814 filed Jan. 25, 1985, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a method for the preparation of emulsions of oil in water and more particularly the preparation of high internal phase ratio (HIPR) emulsions of viscous oils in water.

Many crude oils are viscous when produced and are thus difficult, if not impossible, to transport by normal methods from their production location to a refinery.

Several methods have been suggested for the transportation of such crudes by pipeline. These include (1) heating the crude and insulating the pipeline, (2) adding a non-recoverable solvent, (3) adding a recoverable solvent, (4) adding a lighter crude oil, (5) forming an annulus of water around the crude and (6) emulsifying the crude in water.

Methods (1)-(4) can be expensive in terms of added components and capital expenditure and method (5) is technically difficult to achieve.

Method (6) whilst superficially attractive presents special difficulties. The dispersion of a highly viscous oil in a medium of much lower viscosity is an unfavorable process on hydrodynamic grounds. This problem is further complicated by the economic requirement to transport emulsions containing relatively high oil phase volumes without sacrificing emulsion fluidity. Mechanical dispersing can lead to the formation of polydisperse or multiple emulsions, both of which are less suitable for transportation.

In the case of a system comprising dispersed spheres of equal size, the maximum internal phase volume occupied by a hexagonally close-packed arrangement is ca 74%. In practice, however, emulsions are rarely monodisperse and it is therefore possible to increase the packing density without causing appreciable droplet distortion. Attempts to increase further the internal phase volume results in greater droplet deformation and, because of the larger interfacial area created, instability arises; this culminates in either phase inversion or emulsion breaking. Under exceptional circumstances, it is possible to create dispersions containing as high as 98% disperse phase volume without inversion or breaking.

Emulsified systems containing 70% internal phase are known as HIPR emulsions. HIPR oil-in-water emulsions are normally prepared by dispersing increased amounts of oil into the continuous phase until the internal phase volume exceeds 70%. Clearly, for very high internal phase volumes, the systems cannot contain discrete spherical oil droplets; rather, they will consist of highly distorted oil droplets, separated by thin interfacial aqueous films.

A useful state-of-the-art review of HIPR emulsion technology is given in Canadian Patent No. 1,132,908.

British Patent Specification No. 1,283,462 discloses a method for producing an oil-in-water emulsion comprising

beating up a mixture of the oil and water together with emulsifying agent in a vessel having a bottom exit to disperse the oil in droplets of an average size of not more than 10 microns in diameter throughout the water to form a concentrated emulsion, continuously withdrawing concentrated emulsion from the bottom exit of the vessel while simultaneously introducing components of the mixture into the top of the vessel to form further concentrated emulsion.

The oils are synthetic polymers or thickened animal or vegetable oils.

The action of the beater results in particle sizes in the dispersed phase of not more than 10 microns in diameter, usually from about 0.5 to 2 microns in diameter. The concentration of surfactant used is relatively high, 4-10% by weight of the total composition.

This results in concentrated, thick, extremely stable emulsions which have thixotropic properties and are useful as vehicles for paints or other coatings.

While U.S. Pat. No. 1,283,462 discloses that the concentrated emulsions are discharged through a short conduit from the emulsifying vessel to a tank in which they are further diluted, the concentrated emulsions are not suitable, nor are they intended, for transportation over long distances through relatively large diameter pipelines such as those used for the transportation of crude oil.

Furthermore, because of their extreme stability these emulsions cannot be, and are not intended to be, readily broken. Thus, they are unsuitable for applications where it is desired eventually to resolve the emulsions into their constituent parts, such as the treatment of crude oil where water must be removed before fractionation in an oil refinery distillation unit.

SUMMARY OF THE INVENTION

We have now discovered a method for the preparation of HIPR emulsions of viscous oils in water in which emulsions are directly prepared from a feedstock initially containing a high volume ratio of oil to water using low energy mixing. Some emulsions are readily pumpable through a pipeline, others are so after dilution. The emulsions or diluted emulsions are of high but not excessive stability. By high but not excessive stability we mean that they are stable following preparation, during transportation and on standing, and can resist various conditions encountered during pipeline flow such as temperature fluctuations and mechanical shearing. However, they can be broken when desired by using an appropriate treatment, for example treatment with an alcohol or a salt.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photomicrograph of a typical HIPR (90%) emulsion stabilized with a 2.5% solution of surfactant No. 10 of Table 2.

FIG. 2 shows the droplet size distribution of HIPR emulsion prepared in accordance with the method of the present invention having a narrow band on monodispersity.

FIGS. 3a and 3b are photomicrographs of further HIPR emulsions.

DETAILED DESCRIPTION

According to the present invention there is provided a method for the preparation of an HIPR emulsion of oil in water which method comprises directly mixing 70 to 98%, preferably 80 to 90%, by volume of a viscous oil having a viscosity in the range 200 to 250,000 mPa.s at the mixing

temperature with 30 to 2%, preferably 20 to 10%, by volume of an aqueous solution of an emulsifying surfactant or an alkali, percentages being expressed as percentages by volume of the total mixture; mixing being effected under low shear conditions in the range 10 to 1,000, preferably 50 to 250 reciprocal seconds in such manner that an emulsion is formed comprising highly distorted oil droplets having mean droplet diameters in the range 2 to 50 microns separated by thin interfacial films.

It is a simple matter to determine by routine tests whether any given surfactant is an emulsifying surfactant within the context of the present invention.

Emulsifying surfactants may be non-ionic, ethoxylated ionic anionic or cationic, but are preferably non-ionic.

Suitable non-ionic surfactants are those whose molecules contain both hydrocarbyl, hydrophobic groups (which may be substituted) having a chain length in the range 8 to 18 carbon atoms, and one or more polyoxyethylene groups containing 9 to 100 ethylene oxide units in total, the hydrophilic group or groups containing 30 or more ethylene oxide units when the hydrophobic group has a chain length of 15 carbon atoms or greater.

Preferred non-ionic surfactants include ethoxylated alkyl phenols, ethoxylated secondary alcohols, ethoxylated amines and ethoxylated sorbitan esters.

Non-ionic surfactants are suitably employed in amount 0.5 to 5% by weight, expressed as a percentage by weight of the aqueous solution.

Insofar as non-ionic and ethoxylated ionic surfactants are concerned, the salinity of the aqueous phase is not material and fresh water, saline water (e.g. sea water) or highly saline water (e.g. petroleum reservoir connate water) may equally be employed.

Suitable cationic surfactants include quaternary ammonium compounds and n-alkyl diamines and triamines in acidic form.

They are suitably employed in amount 0.5 to 5% by weight, expressed as above.

Suitable anionic surfactants include alkyl, aryl and alkyl aryl sulphonates and phosphates.

They are suitably employed in amount 0.5 to 5% by weight, expressed as above.

When alkali is employed, it is believed that this reacts with compounds present in the oil to produce surfactants in situ.

Alkali is suitable employed in amount 0.01 to 0.5% by weight, expressed as above.

Ionic surfactants are more sensitive to the salinity of the aqueous phase, particularly to divalent and trivalent ions found in connate water, and fresh water should be used in connection with these materials.

To overcome this problem and improve salt tolerance, hydrophilic polymers may be added in addition to the surfactant or alkali. Suitable polymers include polyvinyl alcohol, polyethylene oxide, polyvinyl pyrrolidone and polysaccharide biopolymers.

When used with a surfactant these polymers may reduce the quantity of non-ionic surfactant required and/or improve the performance of ionic surfactants.

The quantity of polymer employed is preferably in the range 0.25 to 5% by weight of the aqueous solution.

Within the viscosity range 200-2,000 mPa.s, it has been found possible to prepare oil in water emulsions by other means. For a given mixer, towards the lower limit of this

range almost identical droplet size distributions and mean droplet sizes are obtained from the present and conventional methods. On the other hand, as the upper limit of this range is approached, a deterioration in quality of conventionally produced emulsions occurs, indicated by an increase in mean droplet diameter and distribution broadening, suggesting that the method according to the present invention is superior.

For oil phase viscosities greater than 2,000 mPa.s up to the limits of dispersibility, say 250,000 mPa.s, we believe that only the present method is suitable.

HIPR emulsions of highly viscous oils in water are frequently as much as three to four orders of magnitude less viscous than the oil itself and consequently are much easier to pump through a pipeline and require considerably less energy to do so. Usually the droplet size distribution will be in a narrow range, i.e., the emulsions have a high degree of monodispersity. As shown in FIG. 2, preferably at least 80%, ideally at least 90%, of the oil droplets have a mean droplet diameter of less than 10 microns. Ideally at least 80% of the oil droplets have a mean droplet diameter of between 5 to 10 microns.

For a given mixer, the droplet size can be controlled by varying any or all of the three main parameters: mixing intensity, mixing time and surfactant concentration. Increasing any or all of these will decrease the droplet size.

Temperature is not significant except insofar as it affects the viscosity of the oil.

The oil and water may be mixed under conditions known to be suitable for mixing viscous fluids, see HF Irving and RL Saxton, *Mixing Theory and Practice* (Eds. VW Uhl and JB Gray), Vol. 1, Chapter 8, Academic Press, 1966. Static mixers are also suitable.

A particularly suitable mixer is a vessel having rotating arms. Suitably the speed of rotation is in the range 500 to 1,200 rpm. Below 500 rpm mixing is relatively ineffective and/or excessive mixing times are required.

Suitable mixing times are in the range 5 seconds to 10 minutes. Similar remarks to those made above in respect of the speed range also apply to the time range.

The HIPR emulsions as prepared are stable and can be diluted with aqueous surfactant solution, fresh water or saline water to produce emulsions of lower oil phase volume showing high degrees of monodispersity. The emulsions may be diluted to a required viscosity without adversely affecting stability. Because the narrow size distribution and droplet size are maintained upon dilution the resulting emulsion shows little tendency to creaming. This in turn reduces the risk of phase separation occurring.

The emulsions, particularly when diluted, are suitable for transportation through a pipeline and represent an elegant solution to the problem of transporting viscous oils.

Thus according to a further aspect of the present invention there is provided a method for the transportation of a viscous oil which method comprises the steps of (a) preparing an HIPR emulsion of the oil-in-water type by a method as hereinbefore described, (b) optionally diluting the HIPR emulsion with an aqueous phase to a desired viscosity and/or concentration, and (c) pumping the HIPR emulsion or the diluted emulsion through a pipeline.

The stability of the emulsions reduces the risk of phase separation occurring in the pipeline which would result in a higher pressure drop and a loss in efficiency.

After pipelining, for example from an inland oilfield to a coastal terminal, it may be desirable to tranship the oil

further by tanker. In this case, the emulsion, or even more so, the diluted emulsion, may be partially dehydrated before loading.

Suitable oils for treatment are the viscous, heavy and/or asphaltenic crude oils to be found in Canada, the USA and Venezuela, for example Lake Marguerite crude oil from Alberta, Hewitt crude oil from Oklahoma and Cerro Negro crude oil from the Orinoco oil belt.

Generally the API gravity should be in the range 5° to 20°, although the method can be applied to crude oils outside this API range.

Once transported to a refinery, the heavy crude oil-in-water emulsions must be resolved into their component parts and at this stage, further benefits of the low polydispersity of (diluted) HIPR emulsions may be realized. The lack of sub-micron oil droplets, which are more difficult to resolve and commonly cause effluent problems, may result in a more efficient separation process and a cleaner water phase.

The invention is illustrated with reference to the following Examples and FIGS. 1 to 3 of the accompanying drawings.

EXAMPLES

Lake Marguerite crude oil (LMCO) was used as the oil phase. LMCO is a heavy crude oil (10.3° API, $\eta=19,800$ mPas at 25° C.).

The surfactants used were either commercially available or were samples received from BP Chemicals International or BP Detergents International. 2.5% (wt/wt) surfactant solutions were made up in simulated formation water, see Table 1, except where distilled water is indicated.

Typically, 90% HIPR emulsions were prepared by adding a 90 g sample of LMCO to a 250 ml beaker containing 10 g of 2.5% aqueous surfactant solution. This was then mixed at room temperature (20°±2° C.) using a twin-beater hand-held domestic mixer (Moulinex Model No. 593) operating for one minute at 1000 rpm (speed setting "1") followed by a further one minute period at 1200 rpm (speed setting "2").

The morphology of the emulsions resembles well-drained polyhedral foams as shown in the photomicrograph of a typical HIPR (90%) emulsion stabilized by a 2.5% solution of the surfactant used in Example 10, see FIG. 1.

The appearance of the mixture is indicative of whether aqueous surfactant lamellae (dark-brown color, creamy

texture) or aqueous droplets (lustrous black color, smooth texture) are formed. In the former case, the product is completely water-dispersible, whereas in the latter, it is not. Emulsions of lower oil content can be produced by dilution of the former emulsion with aqueous surfactant solution, fresh water or saline water as previously stated.

During the mixing process leading to lamellae, incorporated films of aqueous surfactant are stretched out and folded throughout the bulk oil, ultimately leading to the complex film structure depicted in FIG. 1.

Droplet size distributions of emulsions prepared in this way were measured using Coulter Counter Analysis (Model TA II, Coulter Electronics, Luton, Beds). A typical droplet size distribution curve is shown in FIG. 2.

Dilution of the HIPR emulsion with additional water releases the oil from its constraining framework and spherical droplets separate. This effect can be seen from the photomicrographs presented in FIG. 3; the different appearance of the concentrated and dilute emulsions is a consequence of different contrast levels. Also evident from the photomicrographs of the diluted HIPR emulsions shown in FIG. 3 is the monodispersity of the emulsions prepared in this manner. FIG. 3(a) represents the emulsion of Example 10 and FIG. 3(b) that of Example 17.

Table 2 contains a list and generalized structures of the surfactants used, and their effectiveness as 2.5% solutions based on the water phase in producing HIPR o/w emulsions, except where other concentrations are indicated.

TABLE 1

Composition of Simulated Formation Water Used in the Preparation of LMCO-in-Water Emulsions	
Salt	[salt] (ppm)
NaCl	20,000
KCl	1,000
MgCl ₂	2,000
CaCl ₂	1,000
NaHCO ₃	500

TABLE 2

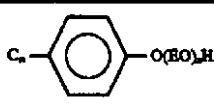
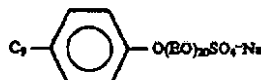
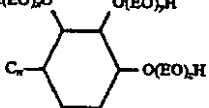
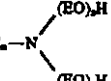
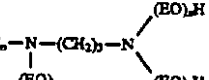
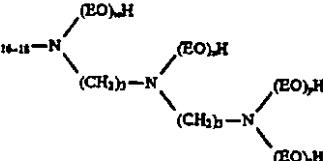
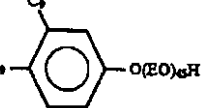
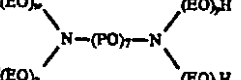
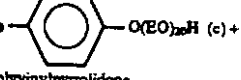
Surfactants used in the Attempted Preparation of 90% o/w Emulsions					
No	Chemical Type	Longest Carbon Chain in Hydrophobe	Average No of EO Groups/ Molecule	O/W Emulsion Formed	Mean Droplet Diameter (microns)
1		13	10	Yes	9.8
2			13	"	6.4
3			15	"	6.0
4			20	"	6.3
5			30	"	9.0
6			30	"	9.0
7			100	"	15.0
8		22	30	No	—
9			20	Yes	7.5

TABLE 2-continued

Surfactants used in the Attempted Preparation of 90% o/w Emulsions					
No	Chemical Type	Longest Carbon Chain in Hydrophobe	Average No of EO Groups/ Molecule	O/W Emulsion Formed	Mean Droplet Diameter (microns)
10	$H(EO)_8O$	12	20	"	12.0
11		16	20	No	—
12	0	18	20	"	—
13		13-17	7	"	—
14	$C_{11-15}-CH-O(EO)_8H$		12	Yes	6.6
15	$ $		20	"	7.5
16	CH_3		40	"	10.5
17		12	15	"	5.4
18		12-14	25	"	5.7
19		12-14	15	"	5.4
20		12-14	15	"	5.6
21		16-18	35	"	7.4
22		18	35	"	6.6
23		16-18	35	Yes	8.5
24		20	45	No	—
25		"21"	28	"	—
26	$C_{12}SO_3Na^+$	12	—	"	—
27	$[C_{12}SO_3^-][HN(EO)_8H]$	12	—	"	—
28	$C_{14}-N(Me)_2^+Br^{(a)}$	14	—	Yes	6.52
29	$NaOH^{(b)}$	—	—	"	23.3
30	 Polyvinylpyrrolidone (mol. wt = 38,000)	13	20	"	11.2
31	Polyisobutene sulphonate (mol wt = 371)			No	
32	Polyisobutene sulphonate ^(c) (mol. wt = 371 + polyvinyl pyrrolidone (mol wt 38,000)			Yes	19.5

^(a)dissolved in distilled water.
^(b)dissolved in distilled water 0.08% by wt concentration
^(c)1.25% by wt concentration of each compound, giving total of 2.5%

I claim:
1. An HIFR emulsion of oil in water comprising 80 to 98% by volume of a viscous oil having a viscosity in the range 200 to 250,000 mPas at the temperature at which the emulsion was formed and 30 to 2% by volume of an aqueous solution of an emulsifying surfactant selected from the

group consisting of non-ionic, ionic and mixtures thereof, percentages being expressed as percentages by volume of the total mixture, wherein the emulsion comprises highly distorted oil droplets having mean droplet diameters in the range 2 to 50 microns separated by thin interfacial films, a high degree of monodispersity, and a narrow range droplet size distribution wherein at least 80% of the oil droplets have a mean droplet diameter of less than 10 microns.

2. An emulsion according to claim 1 wherein the emulsion contains 80 to 90% by volume of the oil.

3. An emulsion according to claim 1 wherein the oil has a viscosity of 2,000 to 250,000 mPas at the temperature at which the emulsion was formed.

4. An oil in water emulsion containing an emulsion according to claim 1 diluted with an aqueous phase.

5. An emulsion according to claim 1 wherein the surfactant is a non-ionic surfactant the molecules of which have a hydrocarbyl, hydrophobic group having a chain length in the range 8 to 18 carbon atoms, and one or more polyoxyethylene groups containing 9 to 100 ethylene oxide units in total, the hydrophilic group or groups containing 30 or more

ethylene oxide units when the hydrophobic group has a chain length of 15 carbon atoms or greater.

6. An emulsion according to claim 5 wherein the surfactant is an ethoxylated alkyl phenol.

7. An emulsion according to claim 1 wherein the surfactant is an ionic surfactant.

8. An emulsion according to claim 7 wherein a hydrophilic polymer is employed in addition to the ionic surfactant.

9. An emulsion according to claim 8 wherein the hydrophilic polymer is polyvinyl alcohol, polyethylene oxide, polyvinyl pyrrolidone or a polysaccharide biopolymer.

10. An emulsion according to claim 1 wherein at least 90% of the oil droplets have a mean droplet diameter of less than 10 microns.

11. An emulsion according to claim 1 wherein at least 80% of the oil droplets have a mean droplet diameter of between 5 to 10 microns.

* * * * *



- (51) International Patent Classification:
B01D 17/04 (2006.01) *F17D 1/17* (2006.01)
B01F 3/08 (2006.01)
- (21) International Application Number:
PCT/IB2010/000317
- (22) International Filing Date:
29 January 2010 (29.01.2010)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/148,306 29 January 2009 (29.01.2009) US
- (72) Inventors; and
- (71) Applicants : **PACHECO, Luis** [CO/CO]; Carrera 14 No. 94-44, Torre A, Piso 6, Bogota DC (CO). **BRICENO, Maria** [VE/PA]; City of Knowledge, Building 231, Clayton, Panama City (PA). **NUNEZ, Gustavo, A.** [VE/PA]; City of Knowledge, Building 231, Clayton, Panama City (PA).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: PIPELINING OF OIL IN EMULSION FORM

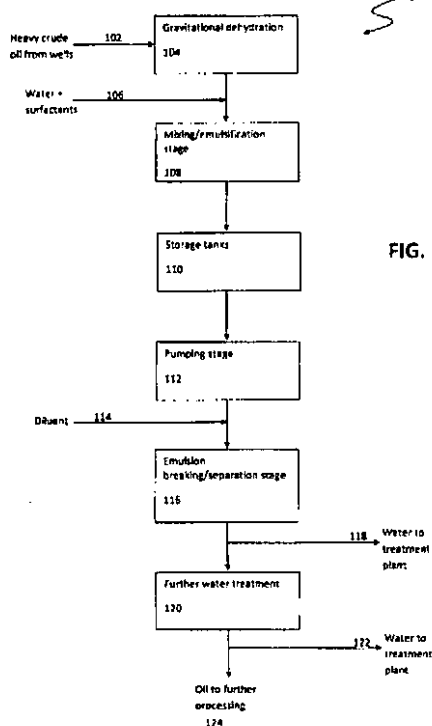


FIG. 1

(57) Abstract: A means for transporting a dispersion of heavy crude oil and water by conventional pipelines. The dispersion is an emulsion prepared by combining production water with crude oil as well as an adequate surfactant system such that the dispersion stabilizes. The dispersion presents a viscosity of less than about 500 cP allowing it to be pumpable and transportable via conventional pipelines. The dispersion, once it arrives at its final destination, is broken or separated by means of one or more suitable diluents such that the remaining oil meets predetermined specifications for further processing, i.e. refining into lighter fractions.

Published:

— with international search report (Art. 21(3))

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY (PCT Rule 43bis.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/IB2010/000317

International filing date (day/month/year)
29.01.2010

Priority date (day/month/year)
29.01.2009

International Patent Classification (IPC) or both national classification and IPC
INV. B01D17/04 B01F3/08 F17D1/17

Applicant
PACHECO, LUIS

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA:



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Date of completion of
this opinion

see form
PCT/ISA/210

Authorized Officer

Redecker, Michael

Telephone No. +49 89 2399-2286



**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/IB2010/000317

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:
- ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).
2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing filed or furnished:
- a. (means)
- ☐ on paper
 - ☐ in electronic form
- b. (time)
- ☐ in the international application as filed
 - ☐ together with the international application in electronic form
 - ☐ subsequently to this Authority for the purposes of search
4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
5. Additional comments:

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	<u>5, 10, 15-17, 20</u>
	No: Claims	<u>1-4, 6-9, 11-14, 18, 19</u>
Inventive step (IS)	Yes: Claims	
	No: Claims	<u>1-20</u>
Industrial applicability (IA)	Yes: Claims	<u>1-20</u>
	No: Claims	

2. Citations and explanations

see separate sheet

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/B2010/000317

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial
applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

- D1 US 528 001 A
- D2 EP 0 414 424 A2 (BRITISH PETROLEUM CO PLC [GB]) 27 February 1991 (1991-02-27)
- D3 US 5 863 301 A (GROSSO JORGE LUIS [CO] ET AL) 26 January 1999 (1999-01-26)
- D4 US 4 821 757 A (HAYES MICHAEL E [US] ET AL) 18 April 1989 (1989-04-18)
- D5 WO 81/02024 A1 (LANKO INC [US]) 23 July 1981 (1981-07-23)
- D6 US 5 354 504 A (RIVAS HERCILIO [VE] ET AL) 11 October 1994 (1994-10-11)

1. Novelty

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-4, 6-9, 11-14, 18, 19 is not new in the sense of Article 33 (2) PCT.

1.1 The document D1 discloses (the references in parentheses applying to this document) a process for the production of crude-oil-in-water emulsions for pipeline transmission (descr. col. 1, l. 25-37), the emulsions comprising from 15% to 60% water (cl. 1). Following transport, the emulsions are broken (descr. col. 17, l. 5-25).

Example XVIII discloses a unimodal emulsion with droplet size $d=34$ microns, while example XIX discloses a bimodal emulsion with $d_1=69.9$ microns and $d_2=54.9$ microns, which shows a reduced viscosity of 140 cp.

D1 further teaches that the viscosity of bimodal emulsions can be further reduced by optimising the maximum packing fraction of oil droplets (descr. col. 41, l. 59-col. 42, l. 42).

Therefore, the disclosure of document D1 seems to anticipate the subject matter of independent claims 1, 13, which are not considered to be novel over D1 in the sense of Article 33(2) PCT.

Dependent claims 2-4, 6, 9, 14, 18, 19 and claims 7, 8, 11, 12 (see the corresponding clarity objections in section VIII) do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty since the respective technical features are disclosed by D1 as cited above.

1.2 The subject matter of claims 1-3, 6-9, 11-14, 18 is anticipated by the disclosure of documents D2-D6, see the corresponding passages cited in the search report.

2. Inventive Step

2.1 Dependent claims 5, 10, 15-17, 20 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step, since the disclosed additional technical features represent routine modifications of the compositions or processes of D1, which are carried out by the skilled person without the involvement of an inventive step.

Re Item VII

Certain defects in the international application

1. The units "barrel", "degrees API" and "inch", used throughout the description and in claims 10, 12, 14, 15, 17, are not recognised in international practice and should be replaced by appropriate SI units (Art. 5 and Rule 10 PCT).

Re Item VIII

Certain observations on the international application

The application does not meet the requirements of Article 6 PCT, because claims 1, 2, 5, 7, 8, 10, 12-14, 17, 20 are not clear.

1. It is clear from the description that the feature of a surfactant is essential to the definition of the invention.

Since independent claim 13 does not contain this feature it does not meet the requirement following from Article 6 PCT taken in combination with Rule 6.3(b) PCT that any independent claim must contain all the technical features essential to the definition of the invention.

Furthermore, said claims disclose a method of transporting, while the feature of an actual transporting step is missing in said claim.

2. The definition of a crude oil content of 45-80% in claim 1 is unclear, since there is no information given whether this refers to the oil phase or to the emulsion (Art. 6 PCT). In order to carry out a meaningful search, it is assumed that the range refers to the crude oil content of the emulsion.

3. In claims 1, 13 the definition of the droplet size distribution from 0.5 up to 500 microns appears to be extremely broad, while the examples show narrow distributions with average values falling into said broad definition. Therefore said claims do not appear to be not supported by the description as required by Article 6 PCT, as their scope is broader than justified by the description and the drawings.

4. Claims 10, 14 do not meet the requirements of Article 6 PCT because the matter for which protection is sought is not clearly defined. The claims attempt to define the subject-matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result.

5. The term "about" used in claims 1, 2, 5, 10, 12-14, 17, 20 is vague and leaves the reader in doubt as to the meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of said claims unclear (Article 6 PCT).

6. Claim 7 is unclear in defining a quaternary ammonium salt as an anionic surfactant, thus raising a contradiction (Art. 6 PCT). Said claim is therefore considered to be non-limiting.

7. Claim 8 is unclear in disclosing the compounds "sodium alkylamines" and "bromide alkylamines", which are not known in the art. Said claim is therefore considered to be non-limiting (Art. 6 PCT).

8. Claims 11, 12 are unclear in disclosing features relating to separation of the emulsion, i.e. process features, while they do not add a limitation to the product, i.e. the emulsion, per se. Said claims are therefore considered to be non-limiting (Art. 6 PCT).

9. The expression "incorporated herein by reference" used throughout the description is unclear (Art. 5 PCT and GL 4.26) and should be deleted.

CONDUCCIÓN POR TUBERÍA DE PETRÓLEO EN FORMA DE EMULSIÓN

RESUMEN-OBJETO Y FINALIDAD DE LA INVENCION

5 Un medio para transportar una dispersión de petróleo crudo y agua mediante tuberías convencionales. La dispersión es una emulsión preparada mediante la combinación de agua de producción con petróleo crudo así como un sistema apropiado de tensoactivos de modo tal que la emulsión se estabiliza. La dispersión presenta una viscosidad de menos de aproximadamente 500 cP que
10 permite que se pueda bombear y transportar vía tuberías convencionales. La dispersión, una vez llega a su destino final, se rompe o se separa mediante uno o más diluyentes apropiados de modo que el petróleo remanente cumpla con las especificaciones predeterminadas para procesamiento adicional, es decir, refinar en fracciones más ligeras.

15

SECTOR: Industria Petrolera, en particular sistemas de conducción para productos viscosos que facilitan el transporte de líquidos viscosos por la modificación de la viscosidad, resultante de la mezcla con otro líquido, y procesos
20 para romper emulsiones.

25

30

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CONDUCCIÓN POR TUBERÍA DE PETRÓLEO EN FORMA DE EMULSIÓN

SOLICITUD RELACIONADA

La presente solicitud reivindica el beneficio de la Solicitud Provisional de E.U. No. 61/148,306 presentada en Enero 29, 2009, que se incorpora aquí en su totalidad como referencia.

CAMPO DE LA INVENCION

La presente invención se relaciona generalmente con el transporte de petróleo crudo. Más específicamente, la presente invención se relaciona con la conducción por una tubería de petróleo crudo en forma emulsificada.

ANTECEDENTES DE LA INVENCION

El procesamiento de petróleo crudo incluye el transporte de petróleo extraído del campo petrolero al área de tanques de una refinería para procesamiento adicional en fracciones más ligeras. Frecuentemente, las áreas de tanques están a distancias significativas de los campos petroleros. Transportar los petróleos crudos pesados se puede lograr mediante cualquier vía diferente incluyendo conducción por tuberías, transporte, y otros medios apropiados para transportar el petróleo crudo.

El transporte de petróleo crudo vía vehículos, tales como carrotanques o camiones de petróleo y similares, es variable en costos y depende extensamente del costo del combustible. Recientemente, este método se ha vuelto cada vez más caro debido al aumento de los precios de la gasolina. Este método se puede llegar fácilmente a costos desorbitados a medida que aumenta la distancia entre el campo petrolero y el área de tanques.

La conducción por tubería de petróleo crudo, ya sea sobre o bajo tierra, es un método más eficiente en costos para transportar el petróleo crudo entre el campo petrolero y el área de tanques. Las tuberías de petróleo están hechas típicamente de tubos de plástico o acero con un diámetro interno típicamente de 10 a 120 cm, o aproximadamente 4 a 48 pulgadas. Las tuberías más profundas están enterradas a una profundidad de aproximadamente 1 – 2 metros, o aproximadamente 3 a 6 pies. El petróleo se mantiene en movimiento mediante estaciones de bombeo a lo largo de la tubería, y usualmente fluye a una velocidad de aproximadamente 1 a 6 m/s.

El petróleo crudo contiene cantidades variables de cera, o parafina, y en climas más fríos puede darse una acumulación de cera en la tubería. Frecuentemente estas tuberías se revisan y se limpian utilizando raspatubos de medición para inspección de tuberías, también conocidos como raspadores. Estos dispositivos se lanzan desde estaciones de lanzamiento de diablo y viajan a través de la tubería para recibirse en cualquier otra estación corriente abajo, limpiando los depósitos de cera y el material que se pudo haber acumulado dentro de la línea.

El petróleo crudo pesado y extra pesado en su forma natural tiene una densidad de aproximadamente 7 hasta aproximadamente 14 grados API, y una viscosidad de aproximadamente 10^3 hasta aproximadamente 10^6 cP a 25 grados centígrados. API, también conocida como gravedad API, significa gravedad del Instituto Americano del Petróleo (por sus siglas en inglés). Es una medida de la densidad relativa del petróleo líquido y la densidad del agua, y se utiliza para comparar densidades relativas de líquidos de petróleo. Por ejemplo, si el API de un petróleo líquido es más de diez, es más ligero que y flota en agua. Si un petróleo líquido tiene una gravedad API mayor que un segundo petróleo líquido, es más ligera que y flota sobre el segundo petróleo líquido.

Debido a la relativamente baja gravedad API y la alta viscosidad del petróleo crudo, toma una cantidad extraordinaria de energía bombear el petróleo crudo en su forma natural, si es que se puede bombear. Similar al transporte vía carrotanques de petróleo, mientras que la distancia entre el campo petrolero y el área de tanques aumenta, la conducción por la tubería de petróleo crudo puro se va volviendo cada vez más costosa y los costos se acumulan.

Es sabido que hacer emulsiones aceite en agua para reducir la viscosidad del petróleo crudo para que bombee mejor, requiere menos energía que las alternativas previamente descritas. Sin embargo, las emulsiones aceite en agua del arte previo típicamente tienen mayores contenidos de agua, de modo que un gran volumen de emulsión debe transportarse para mover el petróleo crudo.

Todavía existe la necesidad de un proceso para colocar una tubería de petróleo crudo pesado en largas distancias desde el campo petrolero hacia las áreas de tanques en donde el petróleo tiene una viscosidad que se puede bombear y es transportable, cumpliendo con las especificaciones del proceso de refinación posterior, es decir, fracciones más ligeras.

RESUMEN DE LA INVENCION

Las realizaciones de la presente invención superan muchas de las deficiencias descritas anteriormente. Las realizaciones de la invención incluyen una dispersión de petróleo crudo pesado y agua que se pueden transportar en tuberías convencionales. La dispersión es una emulsión preparada combinando agua de producción con petróleo crudo así como un sistema de tensoactivos adecuado de modo que la dispersión se estabilice.

En particular, el petróleo crudo pesado se dispersa en la fase acuosa en forma de gotas que tienen tamaños distribuidos entre aproximadamente 0.5 hasta aproximadamente 500 μm . Esta distribución se puede referir como una distribución de tamaño de gota y se puede representar, por ejemplo, en una gráfica de frecuencias como % de volumen o masa como una función del tamaño de gota. Las distribuciones del tamaño de gota se pueden caracterizar mediante parámetros estadísticos tales como la media y la desviación estándar. Una distribución de tamaño de una emulsión puede tener un significado unimodal acerca de que hay un solo valor o pico más frecuente, bimodal (dos valores pico), o polimodal (más de dos picos). Las emulsiones polimodales tienen a ser menos viscosas que las emulsiones unimodales, mientras que las emulsiones bimodales que tienen una proporción de tamaño de partícula grande a tamaño de partícula pequeño cercano a diez, son menos viscosos que los sistemas unimodales o polimodales.

La viscosidad de una emulsión también es una función del contenido de petróleo. Un pequeño incremento de petróleo puede tener un gran impacto en la viscosidad. Modificar la distribución del tamaño de gota como se explica anteriormente, puede compensar un incremento en el contenido de petróleo reduciendo o manteniendo la viscosidad constante.

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Las realizaciones de la presente invención incluyen la preparación de emulsiones unimodales, bimodales y polimodales para maximizar el transporte de petróleo mientras se tienen caídas de presión inferiores a pesar del alto contenido de petróleo. La dispersión unimodal, bimodal o polimodal presenta una viscosidad de menos de aproximadamente 500cP que permite que se pueda bombear y transportar vía tuberías convencionales. La dispersión, una vez llega a su destino final, se rompe o separa mediante uno o más diluyentes apropiados de modo que

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el petróleo remanente cumple con las especificaciones predeterminadas para el procesamiento adicional, es decir, deshidratación y refinación en fracciones más ligeras.

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BREVE DESCRIPCIÓN DE LAS FIGURAS

La FIG.1 es un diagrama de flujo de proceso de acuerdo con una realización de la invención;

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La FIG.2 es un diagrama de flujo de proceso de una etapa de formación de una emulsión unimodal de acuerdo con una realización de la invención;

La FIG. 3 es un diagrama de flujo de proceso de una etapa de formación de una emulsión bimodal o polimodal de acuerdo con una realización de la invención;

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La FIG. 4 es un diagrama de flujo de proceso de un paso de rompimiento de la emulsión de acuerdo con una realización de la invención;

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La FIG. 5 es una gráfica que representa el efecto de la tasa de flujo sobre la distribución del tamaño de gota de emulsiones unimodales de acuerdo con una realización de la invención;

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La FIG. 6 es una gráfica que representa el efecto de la concentración de tensoactivo sobre el tamaño medio de la gota de las emulsiones de acuerdo con una realización de la invención;

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La FIG. 7 es una gráfica que representa el tamaño medio de la gota como función de la potencia de mezcla como el producto de la caída de presión a lo largo del mezclador estático y la tasa de flujo de acuerdo con una realización de la invención;

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La FIG. 8 es una gráfica que representa la viscosidad aparente de una emulsión unimodal 70% medida en una tubería experimental de una pulgada de acuerdo con una realización de la invención;

La FIG. 9 es una gráfica que representa el tamaño medio de gota como función del tiempo y la concentración de tensoactivo de acuerdo con una realización de la invención;

- 5 La FIG. 10 es una gráfica que representa la evolución del tamaño medio de gota de acuerdo con la tasa de flujo en una etapa centrífuga de bombeo de acuerdo con una realización de la invención;

- 10 La FIG. 11 es una gráfica que representa la evolución del tamaño medio de gota en una bomba centrífuga de seis etapas de acuerdo con una realización de la invención;

- 15 La FIG. 12 es una gráfica que representa la distribución del tamaño de gota de dos emulsiones unimodales mezcladas para producir emulsiones bimodales de acuerdo con una realización de la invención;

La FIG. 13 es una gráfica que representa la viscosidad aparente como función del esfuerzo cortante para las emulsiones de la FIG. 12;

- 20 La FIG. 14 es una gráfica que representa el efecto de la adición de un rompiente de la emulsión sobre la separación de agua una y 24 horas después de la dilución utilizando nafta como diluyente; y

- 25 La FIG. 15 es una gráfica que representa el efecto del tipo de diluyente sobre la separación de agua 24 horas después de la dilución.

- 30 El resumen anterior de la invención no pretende describir cada realización ilustrada o cada implementación de la presente invención. Las figuras y la descripción detallada que siguen ejemplifican más particularmente estas realizaciones.

DESCRIPCIÓN DETALLADA DE LAS FIGURAS

- 35 Los procesos de transporte de acuerdo con las realizaciones de la invención incluyen una emulsión de petróleo y agua que se puede bombear y transportar vía tuberías convencionales, y se puede separar fácilmente al llegar a su punto de

destino para procesamiento adicional. Los procesos son eficientes en costos, sin importar la distancia del campo petrolero a los depósitos de petróleo.

En referencia a la FIG. 1, el proceso de conducción por la tubería 100 generalmente incluye una etapa de emulsificación o mezcla 108, un estado de bombeo 112, un estado de rompimiento o separación de la emulsión 116, y al menos un estado de tratamiento de agua 120. En 102, el petróleo crudo pesado tiene una densidad de aproximadamente 7 a aproximadamente 14 grados API y una viscosidad de aproximadamente 10^3 a aproximadamente 10^6 cP se extrae del suelo. El petróleo crudo puede contener sal presente en el agua como sales minerales solubles. Es deseable remover la sal del petróleo crudo para evitar complicaciones en el procesamiento corriente abajo, como en el proceso de refinación. Dado que la sal está presente en el agua como sales minerales solubles, la remoción de agua del petróleo crudo removerá la sal. Por lo tanto, en 104 el petróleo crudo pesado se deshidrata, utilizando deshidratación gravitacional o centrifugas, por ejemplo, para remover el agua.

Una vez que se ha retirado la sal del petróleo crudo, el agua y un sistema de tensoactivos que contiene uno o más surfactantes se combinan con el petróleo crudo en 106. El agua puede ser agua fresca o agua del depósito de petróleo. La fuente de agua preferiblemente tiene una salinidad de aproximadamente 5000 partes por millón (ppm) o menor; sin embargo, también se puede utilizar una salinidad mayor. El sistema de surfactantes puede comprender uno o más tensoactivos aniónicos y/o no iónicos.

Los tensoactivos aniónicos pueden incluir tensoactivos catiónicos tales como sales de amonio cuaternarias, por ejemplo, alquilaminas de sodio o bromo. Los tensoactivos no iónicos pueden incluir, por ejemplo, alcoholes etoxilados primarios o secundarios, y/o alquilfenoles etoxilados. La concentración de tensoactivo puede comprender desde aproximadamente 500 hasta aproximadamente 10,000 ppm, y más específicamente desde aproximadamente 500 a aproximadamente 3,000 ppm.

En la etapa de mezcla o emulsificación 108, el petróleo crudo se mezcla con aproximadamente 55 a 20% p/p de contenido de agua para formar una emulsión aceite en agua. La mezcla se puede realizar entre aproximadamente 35 y aproximadamente 80 grados Celsius. El agua y el sistema de tensoactivos se

combinan con el petróleo crudo pesado en la etapa de emulsificación 108 mediante licuadores o mezcladores estáticos o mecánicos. Un mezclador apropiado, por ejemplo, es el Mezclador Filmics, disponible de la Corporación Primix de Osaka, Japón. El mezclador Filmics y la tecnología se selecciona en la

5 Patente de E.U. No. 5,582,484 titulada "Método de, y Aparato para, agitar líquidos en tratamiento", que se incorpora aquí por referencia en su totalidad. La emulsión se mezcla en la cámara con un canal con una ranura que gira una película de los componentes de la emulsión y crea un campo centrífugo de aproximadamente trece mil gs y más.

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La dispersión o emulsión resultante contiene un contenido de crudo entre aproximadamente 45 y aproximadamente 80 por ciento p/p. La dispersión se puede diluir posteriormente con agua de modo que la dispersión sea manejable, es decir, eficientemente para bombear y transportar, en una tubería convencional

15 tal que el contenido de crudo esté entre aproximadamente 45 y aproximadamente 75 por ciento p/p. La dispersión o emulsión resultante luego se almacena en tanques de almacenamiento a 110, y luego se bombea por la tubería a 112 al depósito de tanques.

20 Una vez la dispersión agua y aceite alcanza su destino, el depósito de tanques, sufre un paso de "rompimiento" o separación 116. En una realización de la invención, etapa 116 es un proceso de dos partes. Primero, un diluyente con una densidad de aproximadamente 25 y 62 grados API se adiciona a 114 a la dispersión para facilitar la separación de la emulsión, y para reducir la densidad y

25 la viscosidad del petróleo de modo que el petróleo sea apropiado para uso y combustible para ebulliciones en la refinación. Segundo, se adiciona una solución básica a una concentración de aproximadamente 0.1 a aproximadamente 0.3% de la dispersión para producir el rompimiento o ruptura de la emulsión, y la separación de la fase de petróleo crudo de la fase acuosa. Esta solución básica

30 puede ser, por ejemplo, una solución de hidróxido de sodio o una amina, tal como monoetanolamina o trietanolamina. Esta solución básica causa que el petróleo y los diluyentes coalescan y se separen del agua.

La fase de petróleo se diluye a partir de la fase original de petróleo crudo, y

35 tiene un contenido de agua de aproximadamente 25% o menos. La densidad resultante de la fase de petróleo es desde aproximadamente 15 grados API a aproximadamente 20 grados API, y preferiblemente aproximadamente 18 grados

AAA

API. La fase de agua tiene un contenido de crudo de aproximadamente 5% o menos. El agua de la fase de agua se envía entonces a una instalación de tratamiento de agua en 118 para su recuperación y reutilización. Puede separarse más agua de la fase de petróleo en 120 usando procesos de deshidratación tales como separadores y deshidratadores gravitacionales y/o electrostáticos de tal manera que la fase de petróleo se encuentre dentro de las especificaciones de densidad y viscosidad para procesamiento adicional. Esta agua adicional separada puede también enviarse a una instalación de tratamiento de agua en 122 para su recuperación y reutilización.

10 En una realización de la invención, haciendo referencia a la FIG. 2, una etapa de emulsificación 200 comprende la formación de una emulsión unimodal. La etapa de emulsificación unimodal 200 incluye generalmente un suministro o tanque 202 de petróleo crudo pesado (HCO, por sus siglas en inglés) y un suministro o tanque de agua 204. El agua del suministro de agua 204 se mezcla
15 opcionalmente con uno o más tensoactivos de un suministro o tanque de tensoactivos 206 en el mezclador 208. El agua que opcionalmente contiene tensoactivos se combina entonces con el petróleo crudo pesado del suministro de HCO 202 en el mezclador 210 para formar una emulsión unimodal. Opcionalmente, puede combinarse más agua del suministro de agua 204 con la
20 emulsión unimodal en el mezclador 212. La emulsión unimodal se almacena posteriormente en el tanque de emulsión o tanque de reserva 214. Los mezcladores 208, 210, y 212 pueden ser mezcladores dinámicos, mezcladores estático-dinámicos, o mezcladores estáticos como se describe *supra*.

Otra realización alternativa de la invención es la fabricación de emulsiones
25 bimodales o polimodales que emplean dos líneas de fabricación. Por ejemplo, una línea maneja aproximadamente 60 a aproximadamente 90% del flujo total y produce una emulsión que tiene un modo grande de aproximadamente 20 a aproximadamente 80 μm . La segunda línea puede manejar aproximadamente 40 a aproximadamente 10% del flujo total y produce una emulsión que tiene un modo
30 pequeño de aproximadamente 0,5 a aproximadamente 10 μm . Las dos líneas se combinan para producir un único camino o corriente de flujo de la emulsión que tiene un contenido de petróleo crudo de aproximadamente 60 a aproximadamente 85% y una distribución de tamaño de gota bimodal o polimodal. Las emulsiones se forman mediante mezcladores dinámicos, mezcladores estático-dinámicos, o
35 mezcladores estáticos o mezcladores mecánicos como se describió *supra*. La emulsión bimodal o polimodal puede también almacenarse en tanques de almacenamiento y bombearse mediante una tubería a un depósito de petróleo.

AAZ

Haciendo referencia a la realización de ejemplo que se ilustra en la FIG. 3, una etapa de emulsificación 300 comprende la formación de una emulsión bimodal o polimodal. La etapa de emulsificación 300 incluye generalmente dos o más suministros o tanques de HCO 302 y un suministro o tanque de agua 304. En un primer camino 306a, e.g. un camino de emulsión de modo pequeño, ilustrado por una línea sólida, el agua del suministro de agua 304 se mezcla opcionalmente en el mezclador 308 con uno o más tensoactivos del tanque o suministro de tensoactivos 310. El agua que opcionalmente contiene tensoactivos se combina posteriormente con petróleo crudo pesado del primer tanque de HCO 302a en el mezclador 312 para formar una emulsión de modo pequeño. En un segundo camino 306b, e.g. una emulsión de modo grande, ilustrada por una línea punteada, el agua del suministro de agua 304 se mezcla opcionalmente en el mezclador 314 con uno o más tensoactivos del suministro o tanque de tensoactivos 316. El agua que opcionalmente contiene tensoactivos se combina posteriormente con petróleo crudo pesado de un segundo tanque de HCO 302b en el mezclador 318 para formar una emulsión de modo grande. El camino de emulsión de modo pequeño 306a y el camino de emulsión de modo grande 306b se combinan posteriormente con agua del suministro de agua 304 en el mezclador 320 para formar una emulsión bi- o polimodal que posteriormente se almacena en un tanque de emulsión o tanque de reserva 322. Los mezcladores 308, 312, 314, y 318 pueden comprender mezcladores dinámicos, mezcladores estático-dinámicos, o mezcladores estáticos o mezcladores mecánicos como se describió *supra*.

Cuando la emulsión llega a su destino para procesamiento adicional, la emulsión se separa o se rompe. En una realización de la invención, para romper la emulsión se adiciona un diluyente con una densidad de aproximadamente 25 a aproximadamente 62 grados API y se adiciona un paquete tensoactivo o un agente de ruptura de la emulsión a la dispersión de petróleo en agua. La emulsión se rompe, separándose parte o casi todo el contenido de agua. El paquete tensoactivo o el agente de ruptura de la emulsión puede comprender cualquier sustancia comercial que produzca de manera suficiente una separación aceptable de agua del petróleo.

Haciendo referencia de manera específica a la realización ejemplar que se ilustra en la FIG. 4, una etapa de separación 400 puede incluir de manera general el tanque de emulsión 214 de la FIG. 2 ó 322 de la FIG. 3, uno o más suministros o tanques de aditivo de ruptura 402, y un tanque diluyente 404. La emulsión uni-, bi-, o polimodal del tanque de emulsión 214, 322 se combina en el mezclador 406

con un primer aditivo de ruptura del primer tanque de aditivo de ruptura 402a y uno o más diluyentes del tanque de diluyente 404. Puede combinarse un segundo aditivo de ruptura opcional de un segundo tanque de aditivo de ruptura 402b con la emulsión separada en el mezclador 408. La emulsión separada puede ser
 5 almacenada o enviada al tanque de separación 410 para procesamiento adicional y separación. Los mezcladores 406 y 408 pueden comprender mezcladores dinámicos, mezcladores estático-dinámicos, o mezcladores estáticos o mezcladores mecánicos como se describe *supra*.

10 Como se discutió en la sección de Resumen, las dispersiones de la presente invención incluyen petróleo crudo pesado dispersado dentro de la fase de agua como gotas que tienen tamaños distribuidos, o una distribución de tamaño de gota, entre aproximadamente 0,5 a aproximadamente 500 μm . Puede hacerse referencia a esta distribución como una distribución del tamaño de gota y
 15 puede representarse, por ejemplo, en una gráfica de frecuencia como % de volumen o masa de las gotas de la emulsión como una función del tamaño de gota. Las distribuciones del tamaño de gota pueden caracterizarse mediante parámetros estadísticos tales como un valor promedio y una desviación estándar. Una distribución de tamaño de una emulsión puede ser unimodal lo que significa
 20 que hay un único valor o pico más frecuente, bimodal (dos valores pico), o polimodal (más de dos picos). Las emulsiones polimodales tienden a ser menos viscosas que las emulsiones unimodales, mientras que las emulsiones bimodales que tienen una relación de tamaño de gota grande a tamaño de gota pequeña cercana a diez, son menos viscosas que los sistemas unimodales o polimodales.

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La viscosidad de una emulsión es también una función del contenido de petróleo. Un pequeño incremento de petróleo puede tener un fuerte impacto sobre la viscosidad. Modificar la distribución del tamaño de gota como se explicó anteriormente puede compensar el incremento en el contenido de petróleo al
 30 reducir o mantener constante una viscosidad.

Las FIGS. 5-7 ilustran los resultados del ensayo de la formación. La FIG. 5 ilustra el efecto de la tasa de flujo en la distribución del tamaño de gota. El tamaño de gota de una emulsión unimodal que contenía 80% de petróleo crudo pesado y
 35 6000 ppm de tensoactivo mezclado en un mezclador estático de una pulgada (2,54 cm) se midió a tasas de flujo de 250, 350, 480, y 580 barriles por día. De

manera típica, las menores tasas de flujo de manera típica resultaron con una distribución más amplia con un tamaño de gota pico más grande que las tasas de flujo mayores. Las tasas de flujo mayores tuvieron de manera típica una distribución más estrecha

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Haciendo referencia a la FIG. 6, se graficó el efecto de la concentración de tensoactivo sobre el tamaño promedio de gota de una emulsión unimodal. El tamaño promedio de gota de una emulsión unimodal que contenía 80% de petróleo crudo pesado con diferentes niveles de tensoactivo mezclado en un
10 mezclador estático de 1" (2,54 cm) se midió a una tasa de flujo de 424 barriles por día. El tamaño promedio de las gotas disminuyó a medida que las concentraciones de tensoactivo aumentaron de 500 a 3500 ppm.

Haciendo referencia a la FIG. 7, se graficó el tamaño promedio de gota de
15 diversas emulsiones como función del poder de mezcla expresado como caída en la presión a través del mezclador estático multiplicado por la tasa de flujo. Se midieron las emulsiones que contenían 80% de HCO con 1000 y 3000 ppm de tensoactivo, al igual que una emulsión que contenía 85% de HCO con 3000 ppm de tensoactivo, y una emulsión que contenía 90% de HCO con 10.000 ppm de
20 tensoactivo. Para todas las emulsiones, el tamaño promedio de gota disminuyó a medida que el poder aumentaba. Esta gráfica permite determinar las condiciones de proceso para emulsiones de modo grande y pequeño.

La FIG. 8 es una gráfica de la curva de viscosidad para una emulsión
25 unimodal comparando la viscosidad aparente como una función de la velocidad de corte medida a entre 23 y 25 grados Celsius en un bucle experimental de una pulgada (2,54 cm). La emulsión unimodal contiene 70% de HCO. La viscosidad disminuye a medida que la velocidad de corte aumenta.

30 La FIG. 9 ilustra la estabilidad estática de las emulsiones en el tiempo como una función de la concentración de tensoactivo. En particular, se midió el tamaño promedio de gota de una emulsión que contenía 70% de HCO con diversos niveles de tensoactivo (1300, 1500, y 3000 ppm) en el transcurso de 20 días. A medida que la concentración de tensoactivo aumentaba, la estabilidad del

tamaño promedio de gota aumentaba, i.e. el tamaño promedio de gota permanecía inalterado después de 20 días.

Las FIGS. 10 y 11 ilustran la estabilidad dinámica de las emulsiones bombeadas con bombas centrífugas de una y seis etapas. La FIG. 10 es una gráfica de la evolución del tamaño promedio de gota como una función de la tasa de flujo en una bomba centrífuga de una etapa. A medida que la tasa de flujo aumenta, la curva de distribución de tamaño se angosta, y el tamaño pico de gota disminuye. La FIG. 11 es una gráfica de la evolución del tamaño promedio de gota en una bomba centrífuga de seis etapas. La curva de distribución de tamaño se angosta y el tamaño pico de gota disminuye tras la circulación desde la distribución inicial.

La FIG. 12 ilustra las curvas de distribución del tamaño de mezclar dos emulsiones sustancialmente unimodales que tienen picos a 3 y 40 micrómetros respectivamente para producir una emulsión bimodal que tiene una proporción volumétrica de la emulsión de modo pequeño de aproximadamente 20%. La FIG. 13 ilustra que una menor viscosidad de una emulsión bimodal que contiene 76% de HCO se obtiene cuando la proporción volumétrica de la emulsión de modo pequeño es aproximadamente 20%.

La FIG. 14 ilustra el efecto de la adición de uno o más agentes de ruptura de emulsión en la separación de agua empleando Nafta como el diluyente. En particular, se midió el porcentaje de agua separada con base en el agua total en el petróleo para emulsiones de 65% de HCO que contenían 800 y 1200 ppm de tensoactivo. El porcentaje de agua separada es la proporción de toda el agua presente en la emulsión que se ha separado del HCO diluido. Las emulsiones que se rompieron mediante la adición de un agente de ruptura de emulsión comercialmente disponible (representado como W/B) se compararon con aquellas en las que no se había adicionado agente de ruptura de emulsión (representadas como N/B). El efecto se midió una y 24 horas después de la dilución.

La FIG. 15 ilustra el efecto del tipo de diluyente con y sin la adición del agente de ruptura de emulsión. Se graficó el efecto usando el porcentaje de agua separada del petróleo para emulsiones de 65% de HCO preparadas con 800 y 1200 ppm de tensoactivo. Los tipos de diluyentes incluían nafta (NAP) que tenía

un API de aproximadamente 60, y petróleo crudo ligero (LCO) que tenía un API de aproximadamente 33. Los diluyentes se adicionaron en una cantidad para obtener un petróleo crudo diluido que tenía un API de aproximadamente 18. El efecto se midió a las 24 horas de la dilución, puesto que el LCO no produjo ninguna separación de agua 1 hora después de la dilución.

Por lo tanto, la invención señala y resuelve muchas de las deficiencias e inconvenientes identificados previamente. La invención puede expresarse en otras formas específicas sin apartarse de los atributos esenciales de la misma; por lo tanto, las realizaciones ilustradas deben ser consideradas en todos los aspectos como ilustrativas y no restrictivas.

REIVINDICACIONES

Lo que se reivindica es:

- 5 1. Una emulsión de agua y petróleo que puede ser bombeada, que comprende:
 - una fase de agua;
 - una fase de petróleo que comprende petróleo crudo presente en una cantidad de aproximadamente 45 a aproximadamente 80 por ciento en peso; y
 - 10 un tensoactivo presente en una cantidad de aproximadamente 500 a aproximadamente 3000 partes por millón;
 - en donde el petróleo crudo está dispersado dentro de la fase de agua como gotas que tienen una distribución de tamaño de gota entre aproximadamente 0,5 y aproximadamente 500 μm .
- 15 2. La emulsión de la reivindicación 1, en donde una viscosidad de la emulsión es aproximadamente 500 cP (0,5 Pa·s) o menos.
- 20 3. La emulsión de la reivindicación 1, en donde la emulsión comprende una emulsión unimodal.
- 25 4. La emulsión de la reivindicación 1, en donde la emulsión comprende una emulsión bimodal o polimodal.
5. La emulsión de la reivindicación 4, en donde la emulsión comprende una emulsión bimodal que tiene una relación de tamaño de gota grande a tamaño de gota pequeño en un rango de aproximadamente diez a aproximadamente quince.
- 30 6. La emulsión de la reivindicación 1, en donde el tensoactivo comprende uno o más tensoactivos aniónicos, uno o más tensoactivos no iónicos, o ambos.

7. La emulsión de la reivindicación 6, en donde el tensoactivo comprende uno o más tensoactivos aniónicos seleccionados del grupo que consiste de sales de amonio cuaternario.
- 5 8. La emulsión de la reivindicación 7, en donde el grupo que consiste de sales de amonio cuaternario comprende alquilaminas de sodio, alquilamidas bromuro, o ambos.
- 10 9. La emulsión de la reivindicación 6, en donde el tensoactivo comprende uno o más tensoactivos no iónicos seleccionados del grupo que consisten de alcoholes primarios etoxilados, alcoholes secundarios etoxilados, alquifenoles etoxilados, y combinaciones de los mismos.
- 15 10. La emulsión de la reivindicación 1, en donde la emulsión puede separarse mediante la adición de un diluyente que tiene una densidad de aproximadamente 25 y 62 grados API, y una solución básica en una concentración de aproximadamente 0,1 a aproximadamente 0,3 por ciento en peso de la emulsión.
- 20 11. La emulsión de la reivindicación 1, en donde la solución básica comprende una solución de hidróxido de sodio, monoetanolamina, o trietanolamina.
- 25 12. La emulsión de la reivindicación 10, en donde la emulsión es separada de tal manera que la fase de petróleo se diluye hasta un contenido de agua de aproximadamente 25 por ciento en peso o menos, y una densidad resultante de aproximadamente 15 grados API a aproximadamente 20 grados API.
- 30 13. Un método para el transporte de petróleo crudo pesado en forma de emulsión, que comprende:
- proveer una fase de petróleo crudo;
 - proveer una fase de agua; y
 - combinar la fase de petróleo crudo y la fase de agua para formar

una emulsión que tiene un contenido de petróleo crudo de aproximadamente 45 a aproximadamente 80 por ciento en peso,

en donde el petróleo crudo es dispersado en la fase de agua como gotas que tienen una distribución de tamaño de gota entre aproximadamente 0,5 y aproximadamente 500 μm .

14. El método de la reivindicación 13, que comprende además:

transportar la emulsión de una primera ubicación a una segunda ubicación mediante una tubería; y

romper la emulsión en la segunda ubicación de tal manera que la fase de petróleo resultante se diluya hasta un contenido de agua de aproximadamente 25 por ciento en peso o menos, y una densidad resultante de aproximadamente 15 grados API a aproximadamente 20 grados API.

15. El método de la reivindicación 14, en donde romper la emulsión comprende:

adicionar un diluyente que tiene una densidad de aproximadamente 25 y 62 grados API a la emulsión;

adicionar al menos un agente de ruptura de emulsión a la emulsión, en donde el agente de ruptura de emulsión comprende una solución básica a una concentración de aproximadamente 0,1 a aproximadamente 0,3 por ciento en peso de la emulsión.

16. El método de la reivindicación 15, en donde la solución básica comprende una solución de hidróxido de sodio, monoetanolamina, o trietanolamina.

17. El método de la reivindicación 15, en donde el diluyente comprende nafta que tiene un API de aproximadamente 60 grados, petróleo crudo liviano (LCO) que tiene un API de aproximadamente 33 grados, o ambos.

18. El método de la reivindicación 13, en donde la emulsión comprende una emulsión unimodal, bimodal o polimodal.

19. El método de la reivindicación 18, en donde la emulsión comprende una emulsión bimodal formada al:

formar una primera emulsión, de modo pequeño, combinando la fase de agua y una primera fase de petróleo crudo;

5 formar una segunda emulsión, de modo grande, combinando la fase de agua y una segunda fase de petróleo crudo;

combinar la emulsión de modo pequeño, la emulsión de modo grande y la fase de agua formando de este modo la emulsión bimodal.

10 20. El método de la reivindicación 19, en donde la emulsión bimodal tiene una relación de tamaño de gota grande a tamaño de gota pequeño en un rango de aproximadamente diez a aproximadamente quince.

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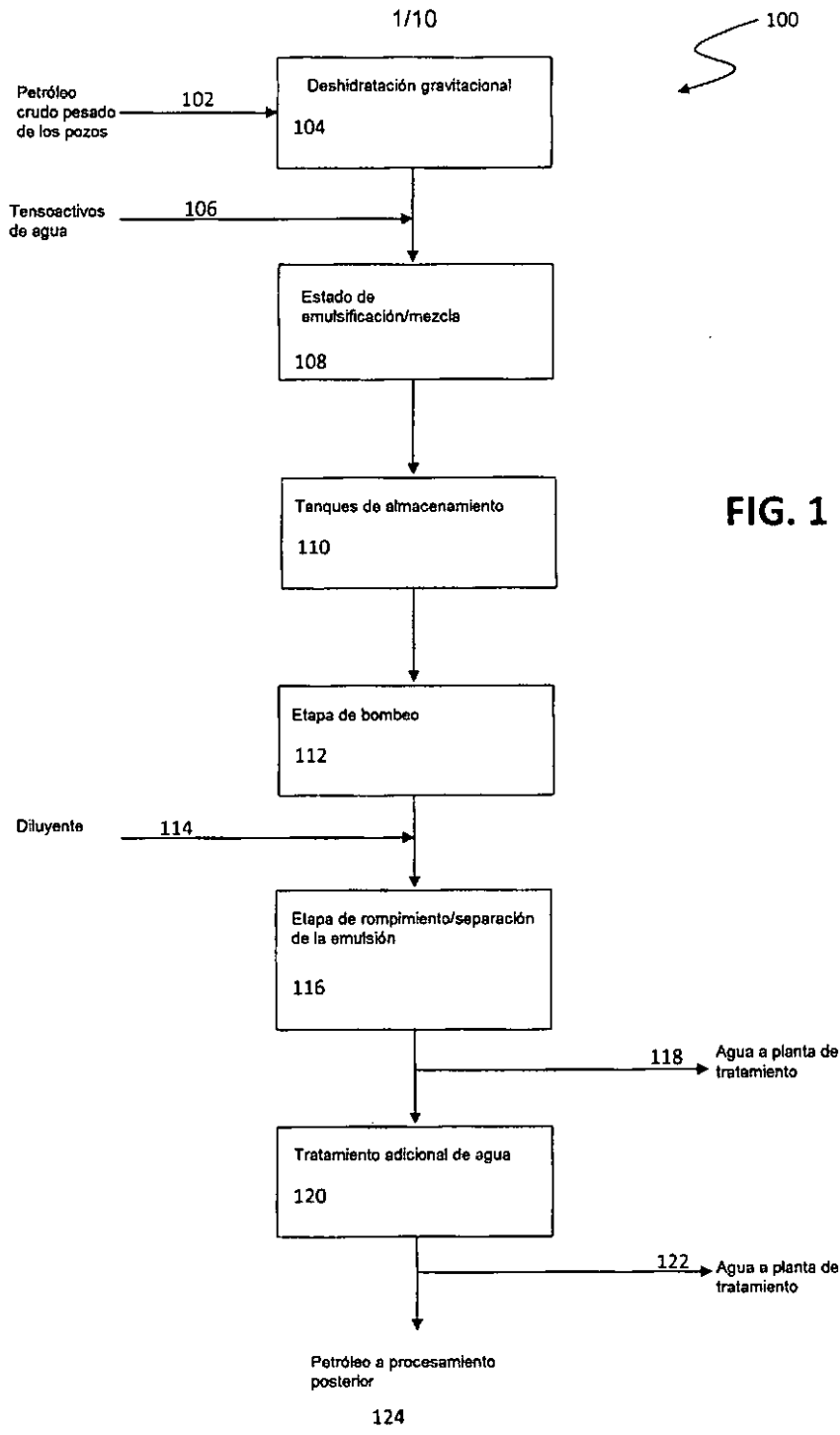


FIG. 1

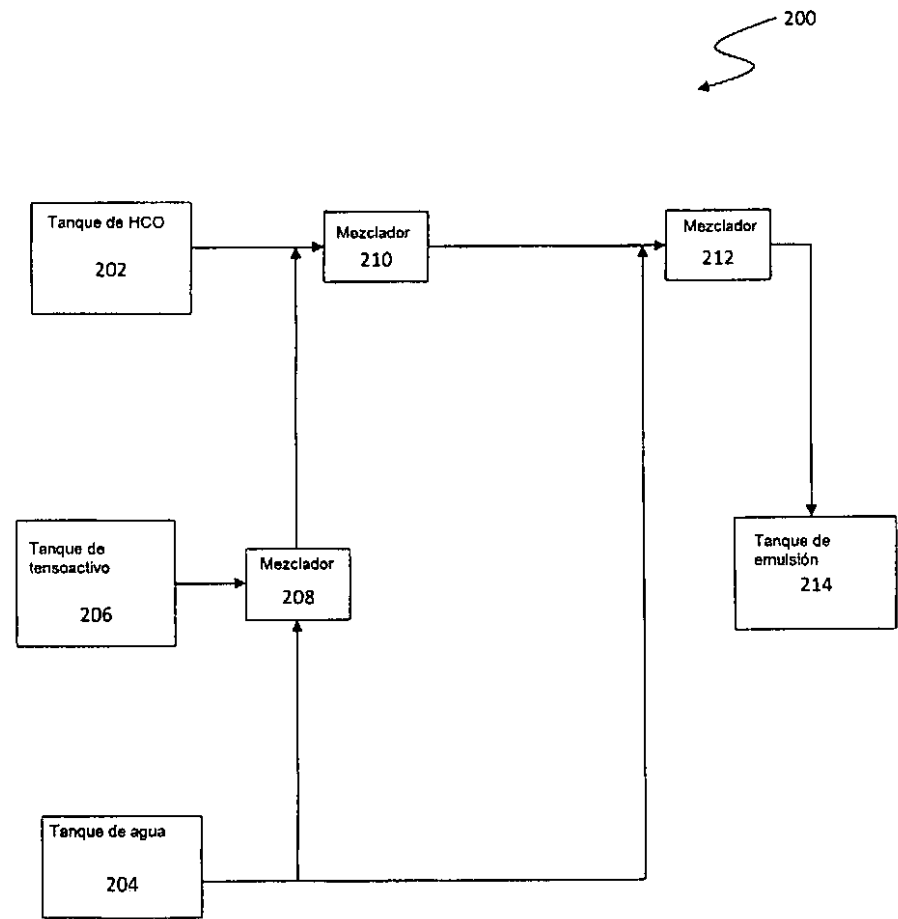


FIG. 2

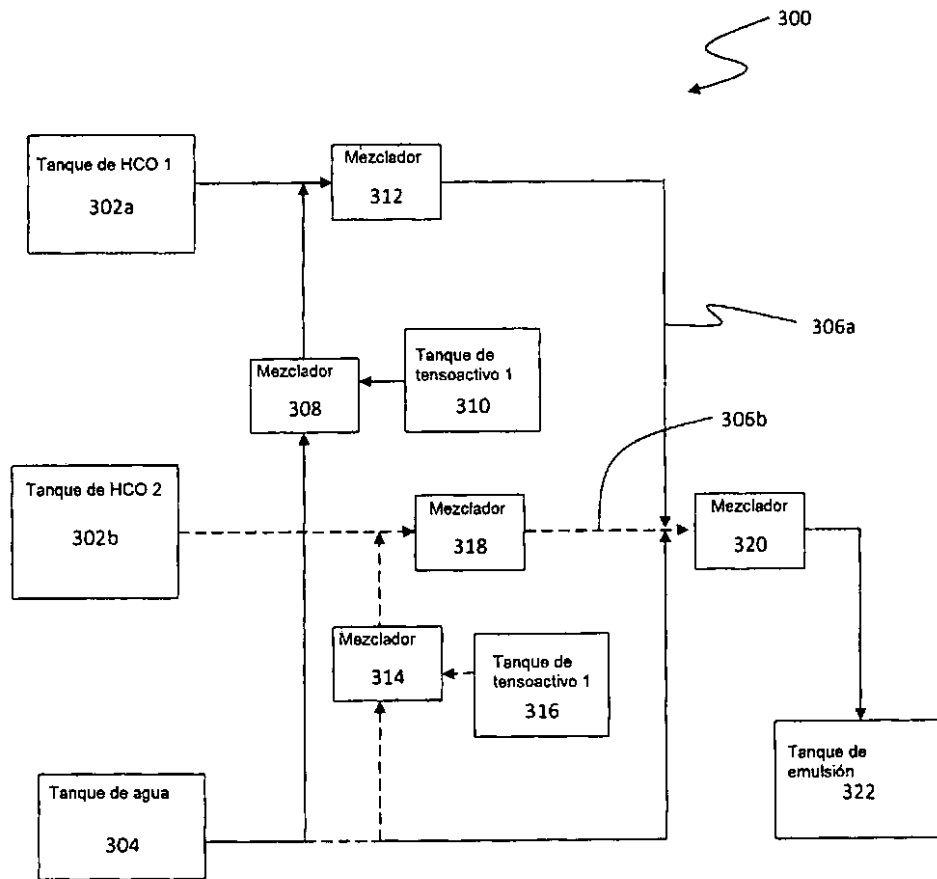


FIG. 3

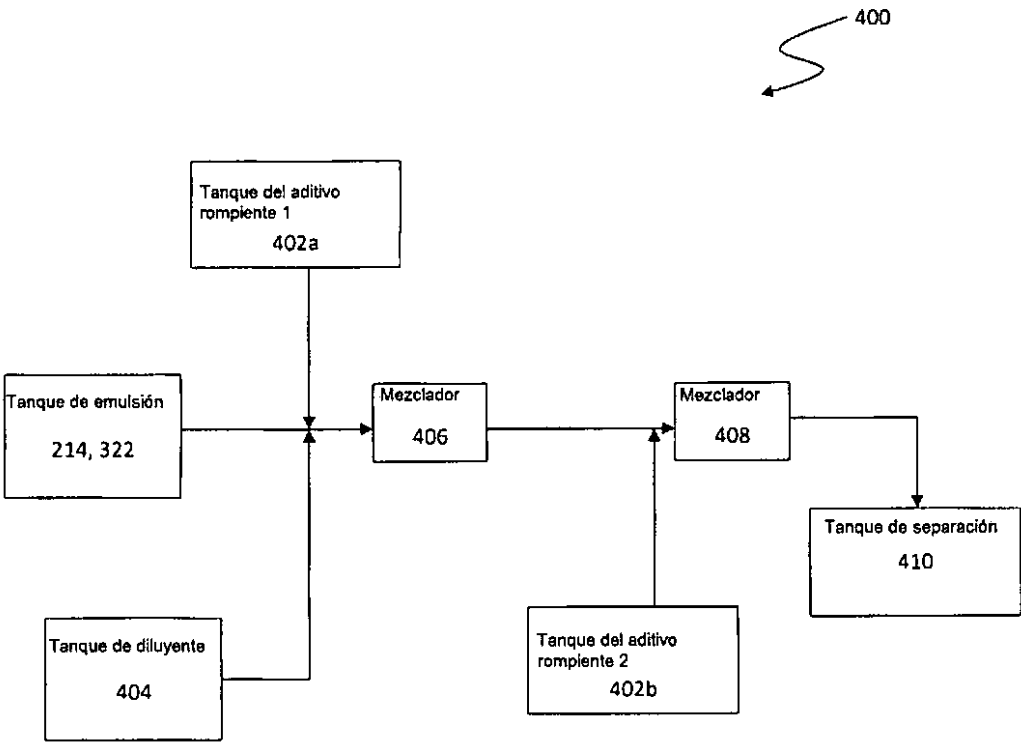


FIG. 4

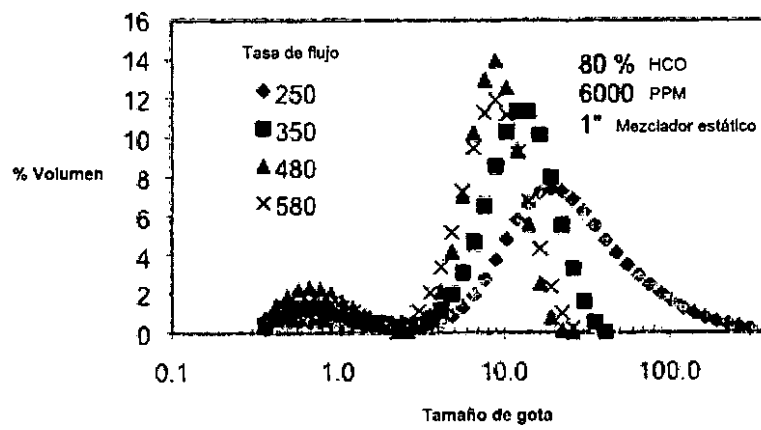


FIG. 5

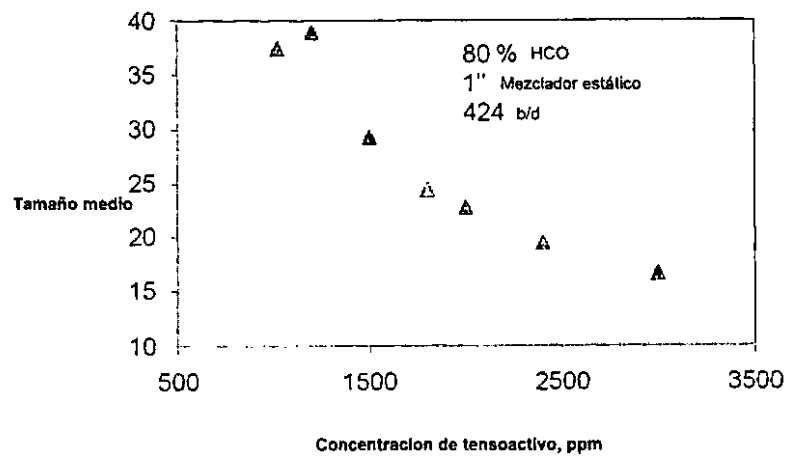


FIG. 6

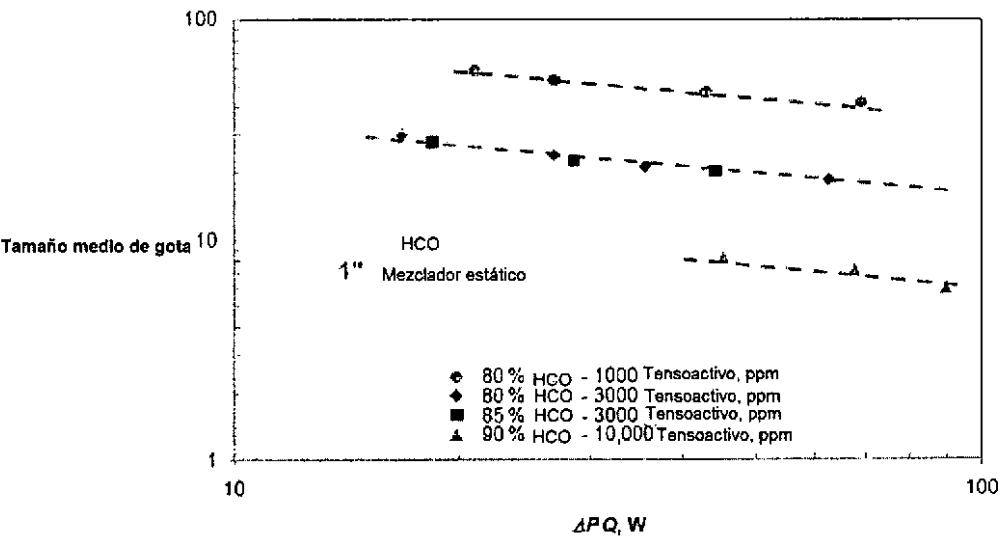


FIG. 7

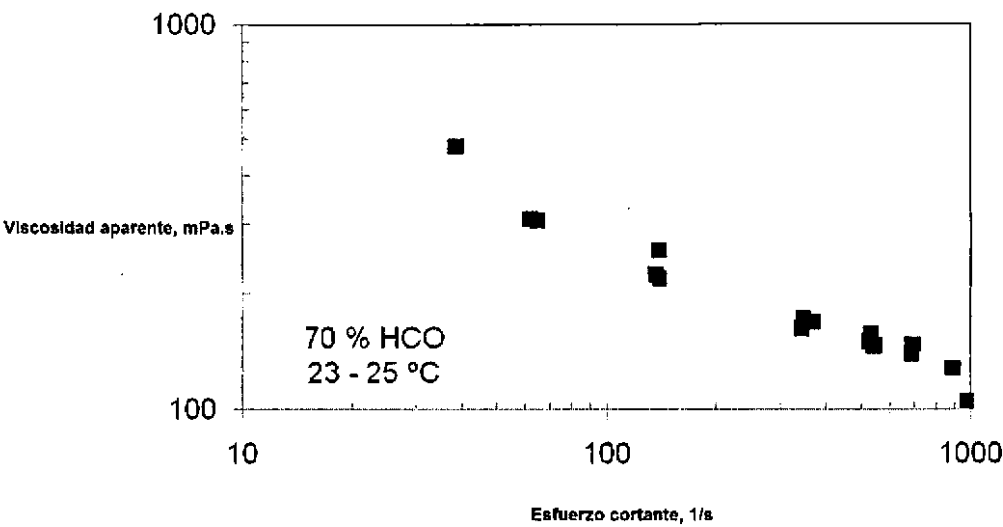


FIG. 8

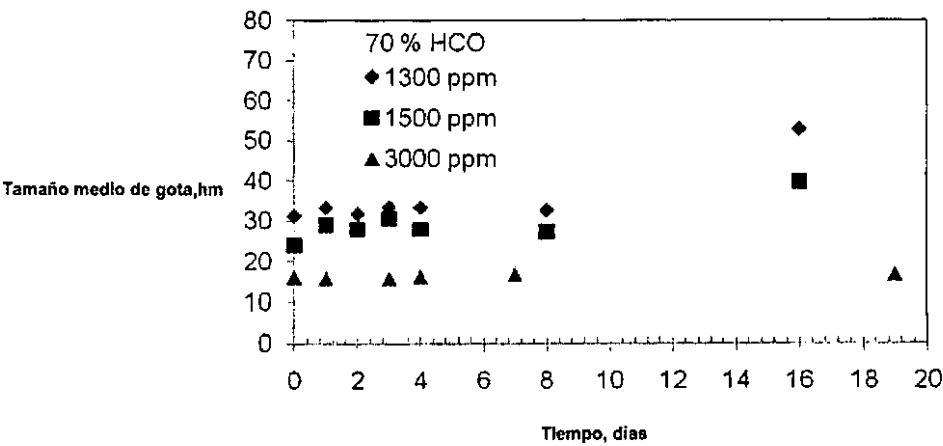


FIG. 9

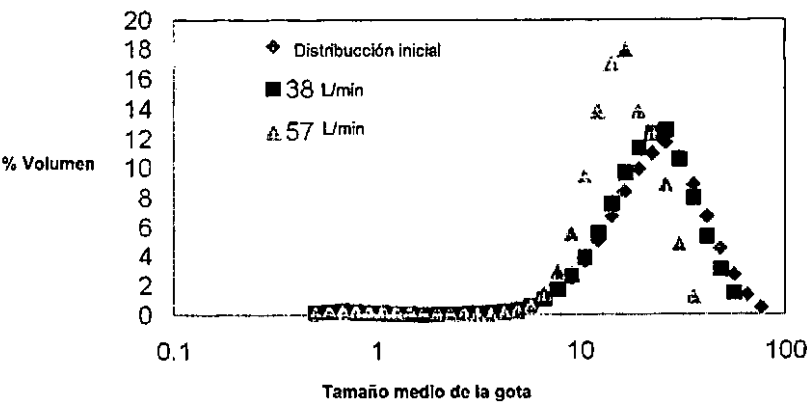


FIG. 10

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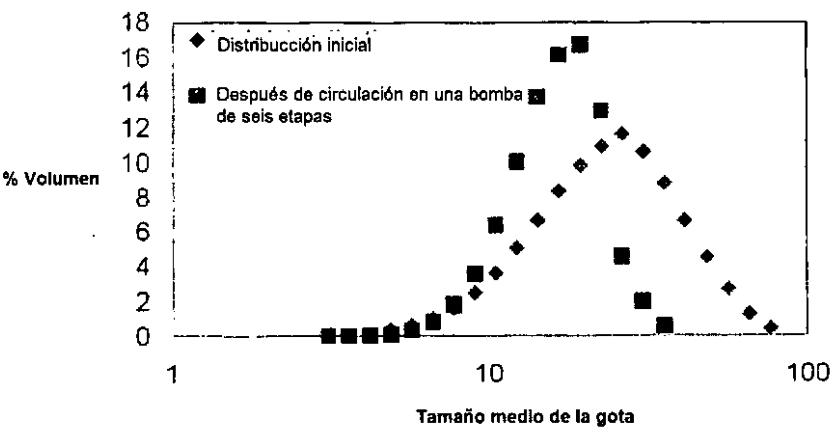


FIG. 11

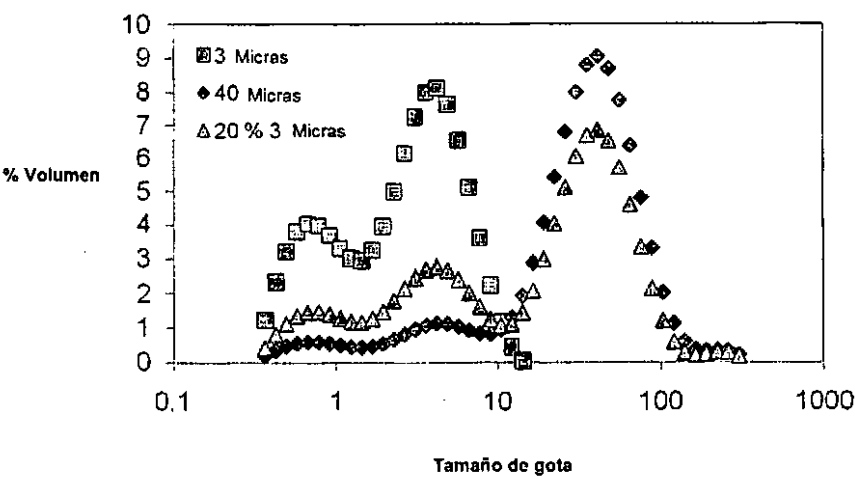


FIG. 12

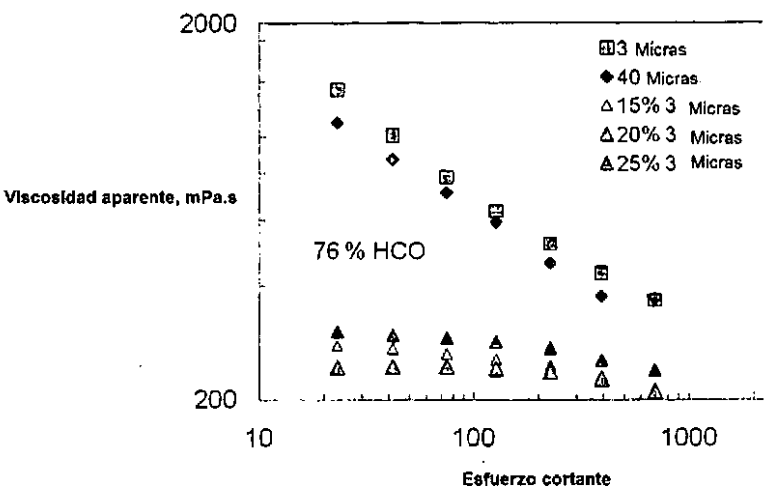
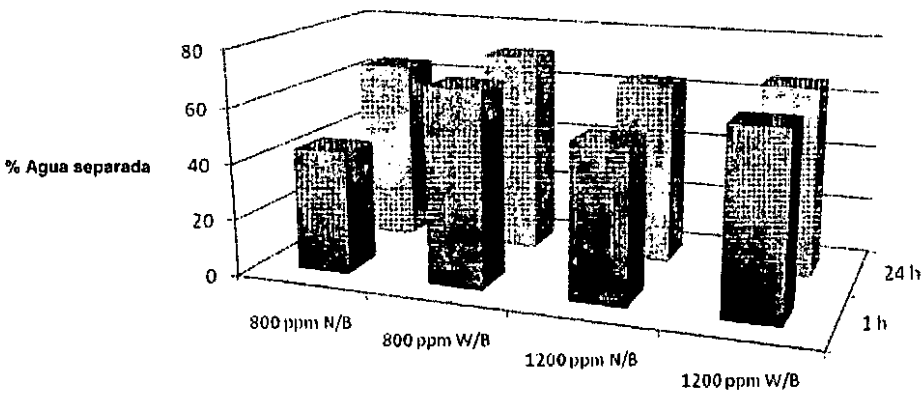


FIG. 13



Diluyente: Nafta

FIG. 14

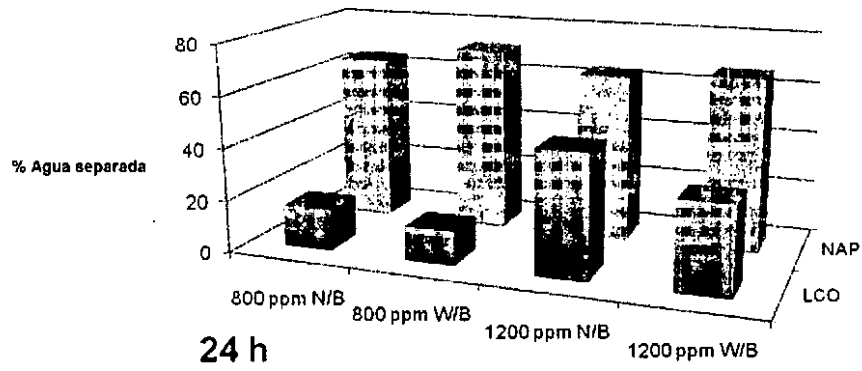


FIG. 15



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PATENTE DE INVENCION ☐

MODELO DE UTILIDAD ☐

Art 33 Decisión 486/00

- ☐ Indicación que solicita una patente
 - ☐ Datos de identificación del solicitante o de la persona que presenta la solicitud
 - ☐ Descripción de la invención
 - ☐ Dibujos de ser estos pertinentes
 - ☐ Comprobante de pago de las tasas establecidas (De ser caso formato de descuento)
- Completa ☐ Incompleta ☐

PATENTE DE INVENCION PCT ☒

MODELO DE UTILIDAD PCT ☐

Art .33 Decisión 486/00, Circular Única

- 1 ☒ Indicación que se solicita una PCT
 - 104 ☒ Copia de la solicitud en español, tal como fue presentada inicialmente (capítulo descriptivo, reivindicatorio, resume)
 - 122 ☒ Dibujos de ser estos pertinentes.
 - 2 ☒ Comprobante de pago de las tasas establecidas (de ser el caso formato de descuento)
- Completa ☒ Incompleta ☐

DISEÑO INDUSTRIAL ☐

(Art. 119 Decisión 486/00)

- ☐ Indicación que se solicita Diseño Industrial
 - ☐ Datos de identificación del solicitante o de la persona que presenta la solicitud
 - ☐ Representación gráfica y fotográfica del Diseño industrial o muestra del material que incorpora el diseño
 - ☐ Comprobante de pago de las tasas establecidas
- Completa ☐ Incompleta ☐

ESQUEMA TRAZADO ☐

(Art. 92 Decisión 486/00)

- ☐ Indicación que se solicita un esquema de trazado
 - ☐ Datos de identificación del solicitante o de la persona que presenta la solicitud
 - ☐ Representación grafica de un esquema de trazado
 - ☐ Comprobante de pago de las tasas establecidas
- Completa ☐ Incompleta ☐