

28 5/1

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Castillo Grau & Asociados
ABOGADOS

**Señora Jefe
DIVISIÓN DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Bogotá, D.C.**

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-094719- -00003-0000

Fecha: 2008-09-24 11:08:53 Dep. 2020 NUECREACIONE
Tra. 17 PATENTABILIDAD Eve: 378 FASENACIONALI
Act. 538 PLTICION Folios: 2

**Re.: Expediente No. 07 94.719
Fase Nacional Solicitud de Patente PCT
a nombre de
SULPHCO, INC.
Código 011 - 378 - 538**

En relación con la solicitud contenida en el Expediente de la referencia y, en particular, con la publicación del extracto de la misma en la Gaceta de la Propiedad Industrial No. 591 de 30 de Abril de 2008, por medio del presente escrito muy respetuosamente me permito solicitarle se sirva proceder a efectuar el **EXAMEN DE PATENTABILIDAD** de la solicitud aquí contenida.

Para tal efecto, acompaño el comprobante de pago por concepto de la tasa respectiva, Recibo No. **75,489.**

De Usted Atentamente,

GERMAN CASTILLO GRAU
T.P. No. 2978 del C.S.J.

29 *[Handwritten signature]*

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 08 - 75,489
FECHA : SEPTIEMBRE 23 DE 2008

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

No. 07-094719-00003-0000
Fecha: 2008-09-24 11:08:53 Dep. 2020 NUECREACIONE
Tra. 11 PATENTE/II Eje: 378 FASENACIONALI
Act. 538 PETICION Folios: 2

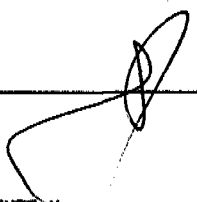
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CASTILLO GRAU Y ASOCIADOS	CONSIGNACION	BANCO DE BOGOTA	062754387	80863856	23/09/2008	3,883,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	420,000.00
		TOTAL :	\$ 420,000.00

SON: CUATROCIENTOS VEINTE MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 07-94719

EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No 591 DE

FECHA 30 DE ABRIL DE 2008 EL TÉRMINO HÁBIL SEÑALADO POR LA LEY

EXPIRA EL 30 DE JULIO DE 2008

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO X

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

2020
Bogotá, D. C., 16 de febrero de 2011

Doctor
Germán Castillo Grau
Representante
Sulphco, Inc.

ASUNTO	Radicación	07-94719
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	103404
	Folios	024

Patente de Invención	☒	Patente de Modelo de Utilidad	☐
Vía Nacional	☐		
Vía PCT (fase nacional)	☒	Cap. I	☒
		Cap. II	☐
No. Sol. Internacional	PCT/US2006/000293		
Fecha de Presentación Internal.	6 de enero de 2006		

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

1. Documentos estudiados

- 1.1. Descripción: Folios: 4 a 15 tal como se radicó inicialmente
- 1.2. Reivindicaciones: Folios 16 a 17 tal como se radicó inicialmente
- 1.3. Prioridad:
 - Fecha 15 de febrero de 2005
 - País US
 - Número 11/059115

2. Objeto de la invención

2.1. Título de la solicitud (*folio 1*)

Enriquecimiento del petróleo mediante tratamientos combinados de ultrasonido y microondas

2.2. Las reivindicaciones 1 a 13 de la solicitud en estudio se refieren a
Un proceso para tratar una materia prima compuesta por petróleo o una fracción del mismo para convertir componentes de esa materia prima en otros productos que tienen puntos de ebullición más bajos que los puntos de ebullición de los mencionados componentes, el cual método comprende:
(a) combinar la mencionada materia prima con un líquido acuoso para formar una emulsión,
(b) exponer esa emulsión a ultrasonido,
(c) a continuación de la etapa (b), irradiar esa emulsión con radiación de microondas para separar esa emulsión en fases acuosa y orgánica, y
(d) recuperar la mencionada fase orgánica.

2.3. El anterior procedimiento busca *mejorar las propiedades de compuestos derivados del petróleo.*

2.4. La Clasificación Internacional de Patentes (IPC) para esta solicitud es
C 10 L 1/04

3. Determinación del Estado de la Técnica

3.1. La fecha que se ha tenido en cuenta para determinar el estado de la técnica es
15 de febrero de 2005

3.2. Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes documentos más relevantes:

Nº	Documento	Título	Fecha de publicación
D1	US 6716358	Demulsification of water in oil emulsions	06.05.2004
D2	US 6086830	Radio frequency microwave energy applicator apparatus to break oil and water emulsion	11.07.2000
D3	US 3616375	Method employing wave energy for the extraction of sulfur from petroleum and the like	26.10.1971
D4	US 4582629	Use of microwave radiation in separating emulsions and dispersions of hydrocarbons and water	15.05.1986
D5	US 5110443	Converting heavy hydrocarbons into lighter hydrocarbons using ultrasonic reactor	05.05.1992

3.3. Los antecedentes refieren

3.3.1. US 6716358 enseña un método para separar emulsiones de aceite en agua

3.3.2. US 6086830 enseña un aparato para romper emulsiones aceite en agua.

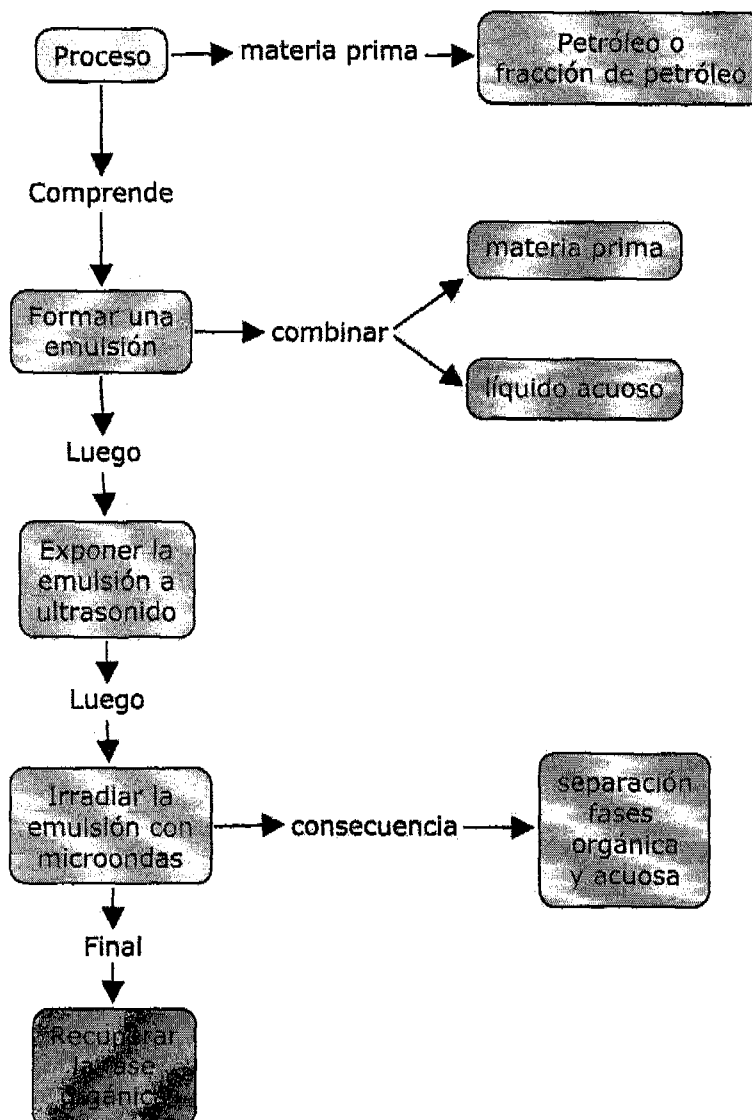
3.3.3. US 3616375 enseña un método para tratar derivados de petróleo empleando energía mediante diferentes longitudes de onda.

3.3.4. US 4582629 enseña un método de separación de emulsiones de aceite en agua mediante radiación por microondas.

3.3.5. US 5110443 relaciona un proceso para tratar emulsiones aceite en agua con ultrasonido

4. Análisis de patentabilidad (Artículo 14 D. 486)

La solicitud colombiana puede sintetizarse de la siguiente forma:



4.1. El documento US 6716358 (D1) relaciona el tratamiento de emulsiones por metodologías de sonicación, método este que consiste en la aplicación de la energía del sonido (generalmente ultrasonidos) para agitar las partículas de una muestra, con diversos fines científicos o industriales (ver todo el documento). Este documento relaciona la preparación de emulsiones (ver ejemplos, principalmente 1 y 2), someter emulsiones a ultrasonido (columna 3, líneas 4 a 13), luego de esto someterlo a un tratamiento de separación el cual puede ser por microondas (columna 3, líneas 14 y siguientes) y recuperar la fase orgánica (columna 3, líneas 19 y siguientes). Los ejemplos también ilustran los procesos y señalan que las materias primas pueden ser derivados de hidrocarburos. Como se demuestra, la anterioridad señala exactamente lo mismo a ser protegido en la presente solicitud.

4.2. US 6086830 enseña un aparato para romper emulsiones aceite en agua. Todo el documento se basa en el principio, según el cual, las ondas microondas pueden separarse emulsiones de hidrocarburos en agua. En la columna 1 (líneas 46 y siguientes) se enseña como la técnica conocida ha demostrado

que las ondas microondas permiten la separación a nivel molecular de las emulsiones de aceite en agua con una gran ventaja en relación a otros métodos y que basado en estos principios desarrollan el aparato para llevar a cabo el proceso ya referido. Luego las etapas de irradiar una emulsión con radiación de microondas para separar esa emulsión en fases acuosa y orgánica, y recuperar la mencionada fase orgánica, resultan del conocimiento promedio de una persona que conozca del arte. Luego afecta el nivel inventivo de la presente solicitud pues al combinarlo con D1 o D5 permite encontrar exactamente lo mismo que se señala en las reivindicaciones de la actual solicitud.

- 4.3. US 3616375 enseña un método para tratar derivados de petróleo empleando, entre otros, ultrasonido y ondas microondas (ver todo el documento). En consecuencia un técnico que conozca del arte podrá considerar el uso de dichas técnicas en emulsiones de hidrocarburo en agua. Además, dichas enseñanzas pueden ser combinadas con los documentos D1 o D2 o D4 o D5.
- 4.4. US 4582629 enseña un método de separación de emulsiones de aceite en agua mediante radiación por microondas. Obsérvese como la anterioridad enuncia el principio de funcionamiento de las ondas microondas que permiten obtener el resultado relacionado en las reivindicaciones de la solicitud en estudio. Este documento combinado con D1 o D5 permiten alcanzar o relacionado en la presente solicitud.
- 4.5. US 5110443 relaciona un proceso para tratar emulsiones aceite en agua con ultrasonido. Enuncia el principio empleado en la primera parte de la solicitud. Al combinarlo con D1 o D2 o D3 o D4 se obtiene lo mismo que el solicitante desea proteger.
- 4.6. Conclusiones. La reivindicación principal de la solicitud en estudio enuncia como característico dos partes: una primera enuncia el tratamiento de una emulsión con ultrasonido; una segunda el tratamiento de una emulsión con microondas. D1 revela las mismas dos partes enumeradas; luego D1 afecta de forma directa a la solicitud en estudio. Los documentos D2, D3 y D4, cada uno de forma independiente y no combinados entre sí, enuncian el principio de la segunda parte, la cual corresponde al tratamiento de una emulsión procedente de hidrocarburos con microondas. Los documentos D5 y D3, cada uno de forma independiente y no combinados entre sí, enuncian el tratamiento con ultrasonido de emulsiones de hidrocarburos. Cómo se puede observar un técnico que conozca del arte puede partiendo de los conocimientos de D3, o a la combinación de dos documentos entre uno cualquiera de D2, D3 o D4, con uno cualquiera entre D3 o D5, para obtener lo mismo sobre lo que el solicitante pretende protección.

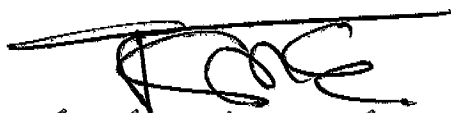
5. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones	Características
D1	US 6716358	1 - 13	Novedad
			Nivel inventivo
D2	US 6086830	1 - 13	Nivel inventivo
D3	US 3616375	1 - 13	Nivel inventivo
D4	US 4582629	1 - 13	Nivel inventivo
D5	US 5110443	1 - 13	Nivel inventivo

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

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.


José Luis Salazar López
Director de Nuevas Creaciones (C)

Concepto Técnico No. 327
Examinador Técnico 202003

25 FEB 2011

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



US006716358B2

(12) United States Patent
Varadaraj**(10) Patent No.: US 6,716,358 B2**
(45) Date of Patent: Apr. 6, 2004**(54) DEMULSIFICATION OF WATER-IN-OIL EMULSIONS**

(75) Inventor: Ramesh Varadaraj, Flemington, NJ (US)
(73) Assignee: ExxonMobil Research and Engineering Company, Annandale, NJ (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: 10/353,735

(22) Filed: Jan. 28, 2003

(65) Prior Publication Data

US 2003/0155307 A1 Aug. 21, 2003

Related U.S. Application Data

(62) Division of application No. 09/803,575, filed on Mar. 9, 2001, now Pat. No. 6,555,009.

(51) Int. Cl.: B01D 17/05

(52) U.S. Cl.: 210/708; 73/61.45; 204/157.15; 210/709; 210/732; 210/748; 436/139; 436/177; 516/143

(58) Field of Search: 73/324, 61.45, 73/61.49; 204/157.15, 164, 157.62; 210/708, 709, 748, 732, 787; 516/143; 436/139, 177

(56) References Cited**U.S. PATENT DOCUMENTS**

2,257,997 A	10/1941	Barnes	252/349
2,864,502 A	12/1958	May	210/72
3,255,571 A	6/1966	Walter et al.	55/P
3,699,051 A	10/1972	Sampeon	252/344
4,283,290 A *	8/1981	Davies	210/643
4,384,977 A *	5/1983	Duke	516/163
4,734,205 A *	3/1988	Jacques et al.	210/708
4,737,265 A *	4/1988	Merchant et al.	208/188
5,251,488 A *	10/1993	Hahnenman et al.	73/861.04
5,487,300 A *	1/1996	Brackett et al.	73/61.59
5,538,628 A *	7/1996	Logan	210/198.1
H1568 H *	8/1996	Huang et al.	210/748
5,885,424 A *	3/1999	Davis et al.	204/157.42
5,951,456 A *	9/1999	Scott	516/195
6,117,682 A *	9/2000	Lynn et al.	436/29

FOREIGN PATENT DOCUMENTS

WO WO 96/05272 2/1996 C10G/33/04

* cited by examiner

Primary Examiner—Peter A. Hruskoci
(74) Attorney, Agent, or Firm—Ramesh Varadaraj; Estelle C. Bakun

(57) ABSTRACT

The invention includes a method for demulsification of water-in-oil emulsions.

19 Claims, No Drawings

US 6,716,358 B2

1
DEMULSIFICATION OF WATER-IN-OIL EMULSIONS

This is a Divisional Application of U.S. Ser. No. 09/803,575 filed Mar. 9, 2001 now U.S. Pat. No. 6,555,009.

FIELD OF THE INVENTION

The invention includes a method for demulsification of water-in-oil emulsions using sonication and recovering oil therefrom. The invention also includes a method for determining the strength of an interfacial film formed at the oil-water interface. The oil of the emulsion can be of any type including crude oils, crude oil distillates, vegetable oils, animal oils, synthetic oils and mixtures thereof.

BACKGROUND OF THE INVENTION

High TAN and asphaltene content crude oils possess the tendency to form stable water-in-crude oil emulsions. Such crude oil typically contains from about 1 to about 60 volume % water. The polar naphthenic acids and asphaltenes in the crude oil stabilize dispersed water droplets. Further, sub-micron size solids like silica and clay, when present in the crude oil, interact with the polar acids and asphaltenes and enhance the stability of the emulsions formed. Formation of stable water-in-crude oil emulsions result in difficulty in separation of water and crude oil. In most cases, known technologies for separation result in an intermediate emulsion rag layer. Further processing of the rag layer is essential to recover the crude oil and discharge the water. The problem is faced both at production facilities and in refinery desalters.

Electrostatic demulsification in the presence of chemical demulsifiers is the most widely used technology for demulsification of water-in-crude oil emulsions.

Gravity settling and centrifugation in conjunction with chemical demulsifiers are also employed.

Recently, a microwave technology (See for example U.S. Pat. Nos. 6,086,830 and 6,077,400) patented by Imperial Petroleum Recovery Corporation has emerged for treatment of hard to treat emulsions especially the rag layer. Thermal flash methods are also known in the art.

SUMMARY OF THE INVENTION

The instant invention includes a method for demulsifying a water-in-oil emulsion comprising the steps of:

- (a) sonicating said emulsion at an energy of about 25 to about 500 watts/cm²;
- (b) separating said emulsion into an oil phase and an aqueous phase; and
- (c) recovering said phases.

The invention may further optionally comprises adding demulsifier to said emulsion prior to or during said sonication step (a).

The invention likewise includes a method for determining the strength of an interfacial film present at the oil-water interface of a water-in-oil emulsion comprising:

- (a) sonicating a series of at least three samples of said water-in-oil emulsion wherein each of said samples is sonicated at an energy of at least about 25 watt/cm² higher than the preceding sample;
- (b) separating each of said sonicated water-in-oil emulsion samples into a water phase and an oil phase;
- (c) determining the percent water separated for each of said samples in said series of samples; and
- (d) determining said strength of said interfacial film which strength corresponds to the energy of sonication at

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which the greatest percentage of water from said series of sample is separated from said water-in-oil emulsion by identifying the energy at which the greatest percentage of water was separated.

The invention also includes a method for separation of a water-in-oil emulsion in a process scheme including an on-line sonicator comprising the steps of:

- (a) collecting a water-in-oil emulsion from said process scheme;
 - (b) sonicating said emulsion, wherein said emulsion is sonicated in a series of at least three samples and wherein each of said samples is sonicated at an energy of at least about 25 watt/cm² higher than the preceding sample;
 - (c) separating each of said samples of sonicated water-in-oil emulsion into a water phase and an oil phase;
 - (d) determining the percent water separated for each of said samples in said series of samples; and
 - (e) determining said strength of said interfacial film which strength corresponds to the energy of sonication at which the greatest percentage of water from said series of sample is separated from said water-in-oil emulsion by identifying the energy at which the greatest percentage of water was separated.
- (f) setting the said on-line sonicator to a sonication energy level corresponding to said determined interfacial film strength; and
- (g) sonicating said water-in-oil emulsion in said on-line sonicator set to said determined interfacial film strength; and
- (h) separating said sonicated emulsion into a layer comprising water and a layer comprising oil.

DETAILED DESCRIPTION OF THE INVENTION

The invention includes a method for recovering oil from a water-in-oil emulsion. In such emulsions, particularly those containing crude oils, the organic acids, asphaltenes, basic nitrogen-containing compounds and solid particles present in the crude form an interfacial film at the water/oil interface. The instant invention affords a way to break the film and demulsify the emulsion, thereby forming a plurality of layers from which oil can be recovered.

The invention may further comprise adding a demulsifier to said water-in-oil emulsion. Use of a demulsifier is believed to weaken the interfacial film present in the emulsion with demulsifier at the oil/water interface. Such a film is weaker than the film formed absent the demulsifier. Thus, use of a demulsifier can lower the sonication energy required to break the interfacial film of the emulsion. One skilled in the art will readily recognize that the sonication energy can be lowered by use of demulsifiers and the advantages associated with their use in hard to break emulsions.

The invention is applicable to any type of water-in-oil emulsion, and is particularly suitable for solids containing water-in-oil emulsions, and is applicable to crude oil emulsions comprising components which may include solids, asphaltenes, organic acids, basic nitrogen compounds and mixtures thereof. Thus, the invention can be applied to water-in-oil emulsions of crude oils, vegetable oils, animal oils, synthetic oils and mixtures thereof. As used herein crude oils include any oils comprising organic acids, and may also contain asphaltenes, solids and basic nitrogen containing compounds. Typically, the solids, if present in the emulsion, will have an average total surface area of ≤ 1500

square microns, more preferably about 25 to about 1500 square microns, even more preferably about 50 to 1500 and most preferably about 100 to about 1500 square microns.

Sonication is the act of subjecting a system to sound (acoustic) waves. The velocity of sound in liquids is typically about 1500 meters/sec. Ultrasound spans the frequency of about 15 kHz to 10 MHz with associated wavelengths of about 10 to 0.02 cm. The invention may be practiced at frequencies of about 15 kHz to about 20 MHz. The output energy at a given frequency is expressed as sonication energy in units of watts/cm². The sonication provided for in the instant invention is typically accomplished at energies of about 25 to about 500 watts/cm².

Following the sonication, the sonicated emulsion is separated by methods such as centrifugation, gravity settling, hydrocyclones, application of an electrostatic field, microwave treatment or combinations thereof or by any other methods known to the skilled artisan for phase separation. The oil may then be recovered as a separate phase. Sonication alone may be sufficient to separate the emulsion into phases or may be combined with another separation method or ceased and the emulsion separated by other methods known to the skilled artisan for phase separation.

The process may be conducted at temperatures of the water-in-oil emulsion of about 20 to about 200° C. and at pressures from ambient to 200 psig (1480.4 kPa).

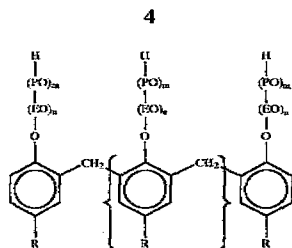
Use of demulsifiers in the invention is optional. If such demulsifiers are utilized, the demulsifiers may be selected from any known demulsifiers that will not degrade during sonication. Such demulsifiers can be readily selected by the skilled artisan. Typically, the demulsifiers will have a molecular weight of about 500 to about 5000, preferably about 500 to about 2000 and a hydrophilic lipophilic balance of above 9 and preferably from 9 to about 35 and most preferably from about 9 to about 15. Demulsifiers which will not degrade during sonication will not contain functional groups such as esters or amides. Demulsifiers will include, but are not limited to those which contain functional groups such as ethers, amines, ethoxylated alcohols, sulfonates and mixtures thereof. A particularly preferred demulsifier is phenolformaldehyde.

The demulsifier will be added to the emulsion prior to or during sonication. The amount of demulsifier to be added will range from about 0.1 to about 5.0 wt % based on the amount of the emulsion. Additionally, a delivery solvent may be employed. Such solvents may include crude oil distillates boiling in the range of about 70° C. to about 450° C., alcohols, ethers and mixtures thereof. Thus, the delivery solvents may be selected from the group consisting of the above.

One skilled in the art will recognize that use of a demulsifier will serve to lower the sonication energy necessary to break the interfacial film of the water-in-oil emulsion. Hence, it may be desirable to utilize a demulsifier. Furthermore, a limited number of emulsions may require the use of a demulsifier due to the strength of the interfacial film. Such emulsions will be readily identifiable to the skilled artisan since sonication alone will not break the emulsion sufficiently.

The delivery solvent will be present in an amount of from about 35 to about 75 wt % in the demulsifier. Thus, when utilized, the delivery solvent will be included in the 0.1 to 5.0 wt % demulsifier added to the emulsion.

A particularly preferred demulsifier is a phenolformaldehyde ethoxylated alcohol having the structure



wherein R is selected from the group consisting of alkanes or alkenes from 8 to 20 carbons, E is CH₂-CH₂ and P is -CH₂-CH₂-CH₂, n ranges from 1 to 5, m ranges from 0 to 5 and x ranges from 3 to 9.

The invention herein described is applicable in refineries as well as in the emulsion-flooding field of operations. In a refinery, water-in-oil emulsions can form during processing of oils or may be present when crudes are shipped to the refinery for processing. Refinery desalter units would be particularly suited for separation of the emulsion once sonication is completed to coalesce dispersed water droplets and recover oil.

Likewise, the invention can be applied to oil produced from subterranean formations where emulsion flooding is used to produce the oil leaving the oil to then be demulsified post-production.

Techniques for separation of the oil and water post sonication include gravity, centrifugation, electrostatic field application, hydrocyclones, microwave, and combinations thereof. The sonication which is utilized prior to separation may likewise serve to separate the emulsion, or may be used in combination with other techniques for phase separation. Such techniques are readily applied by the skilled artisan at the conditions necessary to separate the emulsion into an oil and a water phase. For example, centrifugation can be conducted at 500 to 150,000 g for about 0.1 to about 6 hours or more, and electrostatic field application of about 500-5000 volts/inch for about 0.1 to about 24 hours or more.

The invention is applicable to any water-in-oil emulsion especially those containing components such as organic acids and solids, and which may additionally include asphaltene, basic nitrogen compounds and emulsifiers which are added or naturally present in the emulsion. Thus, the oils forming the emulsion may include crude oils, crude oil distillates, crude oil resids, or oils derived from plant or animal sources such as vegetable oils and animal oils or synthetic oils such as silicone oils. The emulsion may likewise include surfactants or other emulsifiers present in the oil or added for forming the emulsion.

The solids present can be those naturally occurring in such oils such as clay, silica, refinery coke, etc. The solids may likewise have been intentionally added to form the emulsion. When solids are present, they contribute to stabilizing the emulsion and such emulsions are referred to as solids-stabilized emulsions. Solids stabilized emulsions are difficult to demulsify by methods known in the art.

In the method for determining the strength of an interfacial film, a series of samples of the water-in-oil emulsion are treated by applying to the sample sonic energy. At least three samples will form the series. Typically, at least 3 to 5 samples, and more preferably at least 3 to 20 samples, and most preferably 3 to 10 samples will be utilized. The sonic energy is applied to each sample, with each preceding

sample being sonicated at an energy at least about 25 to about 50 watts/cm² higher than the preceding sample. Once sonication is complete, the oil and water phases are separated and the percent demulsified or water phase separated is measured. A maximum amount of demulsification can then be identified and the energy of sonication corresponding to the amount applied to produce the highest quantity of demulsification is equivalent to the strength of the interfacial film of the emulsion. The amount of energy to be applied to the first of the series of samples is in the range of about 25 to 50 watts/cm². If the emulsion is not separable, a demulsifier should be added. A demulsifier, however will be optional in most instances.

The aqueous phase of the emulsion comprises water and may include dissolved inorganic salts of chloride, sulfates and carbonates of Group 1 and 2 elements. Organic salts can also be present in the aqueous phase.

The following examples are meant to be illustrative and not limiting in any way.

EXAMPLE-1

Demulsification of 60/40 Water-In-Crude Oil Emulsion Stabilized by Solids (Centrifugation for Coalescence of Water Droplets of Emulsion)

The general procedure to prepare a 60/40 water-in-crude oil emulsion involved adding 0.15 wt % of solids to the oil followed by addition of water or brine and mixing. A Silverson mixer supplied by Silverson Machines, Inc. East Longmeadow, Mass. was used. Mixing was conducted at 25° C. and at 400 to 600 rpm for a time required to disperse all the water into the oil. Water was added to the crude oil in aliquots spread over 5 additions. When demulsifier was used, it was added to the emulsion at a treat rate of 0.5 wt % demulsifier formulation based on the weight of emulsion and mixed with a Silverson mixer at 400 to 600 rpm for 10 to 15 minutes. A phenol formaldehyde ethoxylated alcohol demulsifier formulation sold by BASF Corporation as Pluradene DB7946 was used to demonstrate the invention.

Centrifugation was conducted at 25° C. using a Beckman L8-80 Ultracentrifuge at 10,000 rpm (7780 g) for 30 minutes to effect separation of the water and oil phases. Sonication was conducted using a Sonifier Model 350. The pulse mode

operating at an output control setting of 4 was used and sonication conducted for 2 minutes. At the control setting of 4 the output energy is about 150 Watts/cm². The frequency of sonication was 20 kHz.

The invention was demonstrated using two crude oils, Korne and Hoosier from West Africa and Canada respectively. Hydrophobic silica sold under the trade name Aerosil R 972 by DeGussa Corporation and hydrophobic bentonite clay (prepared in the laboratory by exposing divided/delaminated clay to crude oil and air oxidation) were used as the silica and clay solids for solids stabilization of the 60/40 water-in-crude oil emulsion.

In a typical experiment 30 to 40 grams of emulsion were weighed into graduated centrifuge tubes and treated as indicated in Table-1. After treatment the tubes were centrifuged and the amount of water that broke out of the emulsion recorded.

Control experiments were those that were not subject to any treatment prior to centrifugation.

Results in Table-1 indicate that sonication by itself and in combination with demulsifier significantly enhance demulsification effectiveness.

TABLE 1

Demulsification of 60/40 Water-In-Crude Emulsion; Centrifugation for Coalescence of Dispersed Water

Crude Oil	Water	Solids	Demulsifier BASF Pluradene	Sonication 150 Watts/cm ² 2	Demulsification % Brine Breakout
Korne	Korne Brine	Silica	None	None	0
Korne	Korne Brine	Silica	0.5 wt %	None	0
Korne	Korne Brine	Silica	None	2 minutes	31
Korne	Korne Brine	Silica	0.5 wt %	2 minutes	97
Korne	Korne Brine	Silica	0.5 wt %	2 minutes	99
Hoosier	Hoosier Brine	Silica	None	None	0
Hoosier	Hoosier Brine	Silica	0.5 wt %	None	37
Hoosier	Hoosier Brine	Silica	None	2 minutes	50
Hoosier	Hoosier Brine	Silica	0.5 wt %	2 minutes	99
Hoosier	Hoosier Brine	Clay	0.5 wt %	2 minutes	99

EXAMPLE-2

Demulsification of 20/80 Water-In-Crude Oil Emulsion (Electrostatic Coalescence of Water Droplets of Emulsion)

The general procedure to prepare a 20/80 water-in-crude oil emulsion involved addition of water or brine to the crude oil and mixing. A Silverson mixer supplied by Silverson Machines, Inc. East Longmeadow, Mass. was used. Mixing was conducted at 25° C. and at 400 to 600 rpm for a time required to disperse all the water into the oil. Water was added to the crude oil in aliquots spread over 5 additions. When demulsifier was used, it was added to the emulsion at a treat rate of 0.5 wt % demulsifier formulation based on the weight of emulsion and mixed with a Silverson mixer at 400 to 600 rpm for 10 to 15 minutes. A phenol formaldehyde ethoxylated alcohol demulsifier formulation sold by BASF Corporation as Pluradene DB7946 was used to demonstrate the invention.

Electrostatic demulsification was conducted using a model EDPT-128™ electrostatic dehydrator and precipitation tester available from INTER-AV, Inc., San Antonio, Tex. Demulsification was conducted at an 830 volt/inch

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potential for 30 to 180 minutes at temperatures of 60 and 85° C. Sonication was conducted using a Sonifier Model 350. The pulse mode operating at an output control setting of 4 was used and sonication conducted for 2 minutes. At the control setting of 4, the output energy is about 150 watts/cm². The frequency of sonication was 20 kHz.

Two crude oils, Kome and Hoosier from West Africa and Canada respectively were utilized. Hydrophobic silica sold under the trade name Aerosil R 972 by DeGussa Corporation was used for solids stabilization of the Hoosier oil.

In a typical experiment 30 to 40 grams of emulsion was weighed into graduated electrostatic demulsification tubes and treated as indicated in Table-1. After electrostatic treatment, the amount of water that separated out of the emulsion was recorded.

Control experiments were those that were not subject to any treatment prior to electrostatic demulsification.

Results in Table-2 indicate that sonication by itself and in combination with demulsifier significantly enhance demulsification effectiveness. Comparison of results in Tables 1 and 2 indicate that laboratory centrifugation was more effective in coalescing the water droplets than the laboratory electrostatic desalter. Field electrostatic desalters operating at higher electrostatic fields are known to improve separation effectiveness over those observed in laboratory instruments.

TABLE 2

Demulsification of 20/80 Water-in-Crude Emulsion; Electrostatic Coalescence of Dispersed Water					
Crude Oil	Water	Solids	Demulsifier BASF Phenadine	Sonication 150 Watts/cm ²	Demulsification % Brine Breakout
Kome	Kome Brine	None	None	None	4
Kome	Kome Brine	None	0.5 wt %	None	75
Kome	Kome Brine	None	None	2 minutes	19
Kome	Kome Brine	None	0.5 wt %	2 minutes	94
Hoosier	Hoosier Brine	Silica	None	None	4
Hoosier	Hoosier Brine	Silica	0.5 wt %	None	5
Hoosier	Hoosier Brine	Silica	None	2 minutes	50
Hoosier	Hoosier Brine	Silica	0.5 wt %	2 minutes	75

Example for Interfacial Film Strength Determination:

A 50/70 water-in-crude oil emulsion was prepared by adding 0.15 wt % of hydrophobic silica solids to a Tulare crude oil followed by addition of Tulare brine and mixing. A Silverson mixer supplied by Silverson Machines, Inc. East Longmeadow, Mass. was used. Mixing was conducted at 25° C. and at 400 to 600 rpm for a time required to disperse all the water into the oil. The brine was added to the crude oil in aliquots spread over 5 additions.

The prepared emulsion was divided into eight samples 6 g each into eight graduated tubes.

Sample #1 was the control sample that was not sonicated.

Samples #2, #3, #4, #5, #6, #7 and #8 were sonicated at 50, 100, 150, 200, 250, 300 and 350 Watts/square cm respectively for 2 minutes each. Sonication was conducted using a Sonifier Model 350 in the pulse mode.

After sonication samples #1 through #8 were centrifuged. Centrifugation was conducted at 25° C. using a Beckman 18-80 Ultracentrifuge at 2,000 rpm (1550 g) for 30 minutes to effect separation of the water and oil phases. After

centrifugation the amount of brine separating out was recorded. Results are shown in Table-3.

TABLE 3

Sample #	Sonication Energy (watts/cm ²)	% Brine Separated
1	None	44
2	50	83
3	100	72
4	150	44
5	200	11
6	250	6
7	300	6
8	350	6

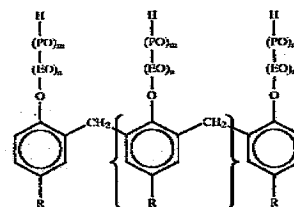
The interfacial film strength is in the range of 50 to 100 watts/cm².

What is claimed is:

1. A method for determining a strength of an interfacial film present at an oil-water interface of a water-in-oil emulsion comprising:

(a) sonicating a series of at least three samples of said water-in-oil emulsion wherein each of said samples is sonicated at an energy of at least about 25 watt/cm² higher than the preceding sample;

(b) separating each of said sonicated water-in-oil emulsion samples into a water phase and an oil phase;



wherein R is selected from the group consisting of alkanes, alkenes, or mixtures thereof from 8 to 20 carbons, E is CH₂-CH₂ and P is -CH₂-CH-CH₂, n ranges from 1 to 5, m ranges from 0 to 5 and x ranges from 3 to 9.

5. The method of claim 1 wherein said demulsifier comprises demulsifier and about 35 wt % to about 75 wt % of a solvent selected from the group consisting of crude oil distillates, alcohols, ethers or mixtures thereof.

6. The method of claim 1 wherein the demulsifier is present in an amount from 0.01 to 5.0 wt % based on the weight of emulsion.

7. The method of claim 1 wherein the oil of said water-in-oil emulsion is selected from crude oil, crude oil distillate, crude oil resid, vegetable oil, animal oil, synthetic oil and mixtures thereof.

8. The method claim 1 wherein the method is conducted at a temperature of about 20 to about 200° C.

9. The method of claim 1 wherein said separation is accomplished by centrifugation, hydrocyclones, microwave, electrostatic field, sonication, gravity settling and combinations thereof.

10. The method of claim 9 wherein said centrifugation is conducted using a field which ranges from 500 to 150,000 g for a time from 0.1 to 6 hours.

11. The method of claim 9 wherein said electrostatic field ranges from about 500 to about 5000 volts per inch for a time from 0.1 to 24 hours.

12. The method of claim 1 wherein said water of said water-in-oil emulsion contains dissolved inorganic salts of chloride, sulfates or carbonates of Group 1 and 2 elements.

13. The method of claim 1 wherein said emulsion contains solids.

14. The method of claim 1 wherein said solids have an average total surface area of <1500 square microns.

15. The method of claim 13 wherein said solids are selected from the group consisting of hydrophobic silica, hydrophobic clay, refinery coke and mixtures thereof.

16. The method of claim 15 wherein said hydrophobic clay is hydrophobic bentonite clay.

17. The method of claim 1 wherein said sonication is conducted at frequencies of about 15 kHz to about 10 MHz.

18. The method of claim 1 wherein said sonication is conducted in continuous or pulse mode.

19. A method for separation of a water-in-oil emulsion in a process scheme including an on-line sonicator comprising the steps of:

(a) collecting a water-in-oil emulsion from said process scheme;

(b) sonicating said emulsion, wherein said emulsion is sonicated in a series of at least three samples and wherein each of said samples is sonicated at an energy of at least about 25 watt/cm² higher than the preceding sample;

(c) separating each of said samples of sonicated water-in-oil emulsion into a water phase and an oil phase;

(d) determining the weight of water separated for each of said samples in said series of samples;

(e) calculating a weight percent of water separated for each of said samples in said series of samples said weight percent is the percent demulsification;

(f) identifying a sample exhibiting maximum percent demulsification from said series of samples and the energy of sonication corresponding to the said sample exhibiting maximum percent demulsification is the strength of the interfacial film of the emulsion.

(g) setting the said on-line sonicator to a sonication energy level corresponding to the interfacial film strength; and

(h) sonicating said water-in-oil emulsion in said on-line sonicator set to interfacial film strength; and

(i) separating said sonicated emulsion into a layer comprising water and a layer comprising oil.

88 A



US006086830A

United States Patent [19]
Kartchner

[11] Patent Number: 6,086,830
[45] Date of Patent: Jul. 11, 2000

[54] RADIO FREQUENCY MICROWAVE ENERGY
APPLICATOR APPARATUS TO BREAK OIL
AND WATER EMULSION

4,855,695 8/1989 Samardzija 339/173
5,498,857 3/1996 Jacquault 219/745

FOREIGN PATENT DOCUMENTS

0327439 8/1989 European Pat. Off. .
19305615 8/1996 Germany .
WO 85/04893 11/1985 WIPO .
WO 94/26844 11/1994 WIPO .

OTHER PUBLICATIONS

C.S. Fang, Bruce K.J. Chang and Peter M.C. Lai, Dept. of
Chem. Eng'g and W.J. Klaile "Microwave Demulsification"
in the publication Chemical Eng'g. Comm., 1988, vol. 73,
pp. 227-239.

Primary Examiner—Kishor Mayekar
Attorney, Agent, or Firm—Jenkins & Gilchrist, P.C.

[21] Appl. No.: 09/295,566
[22] Filed: Apr. 21, 1999

Related U.S. Application Data

[63] Continuation of application No. 08/936,163, Sep. 23, 1997,
Pat. No. 5,914,014.

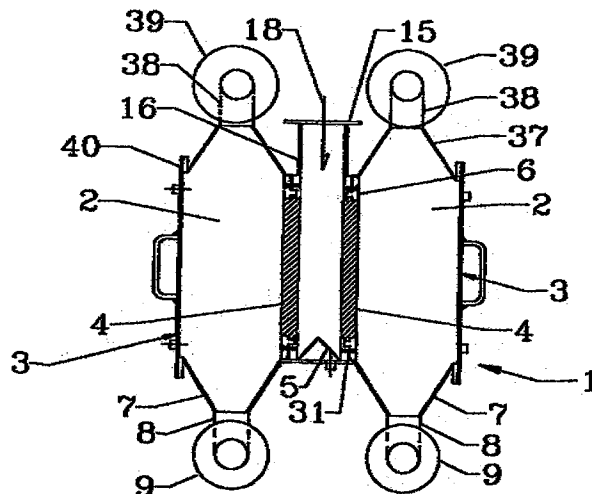
[51] Int. Cl.⁷ B01J 19/08
[52] U.S. Cl. 422/186
[58] Field of Search 422/186

References Cited

U.S. PATENT DOCUMENTS

4,067,683 1/1978 Klaile 431/11
4,174,751 11/1979 Conpton 166/256
4,279,722 7/1981 Kirkbride 204/162 R
4,582,629 4/1986 Wolf 252/348
4,778,970 10/1988 Klaile 219/60.55 D
4,810,375 3/1989 Hudgins et al. 210/112
4,853,119 8/1989 Wolf et al. 210/181
4,853,307 8/1989 Samardzija 210/110.55

12 Claims, 4 Drawing Sheets



U.S. Patent

Jul. 11, 2000

Sheet 1 of 4

6,086,830

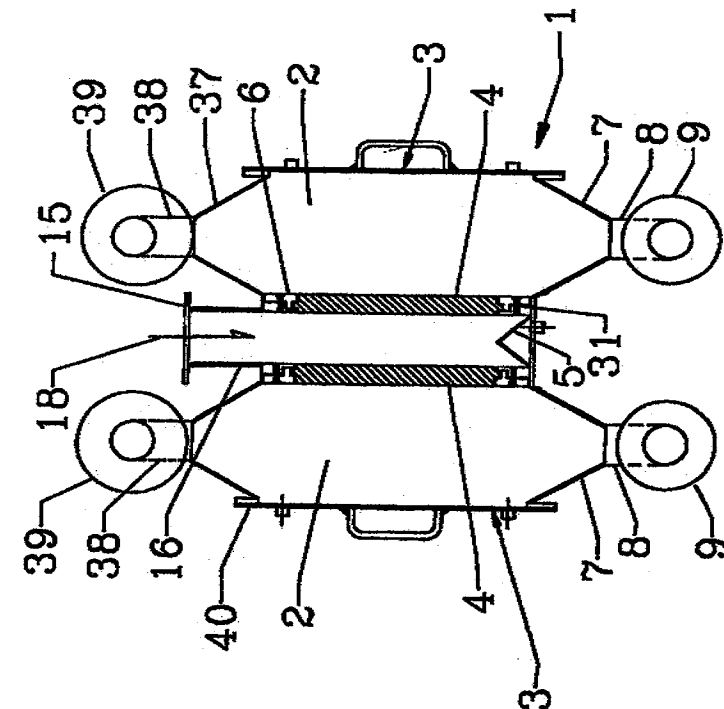


Figure 1

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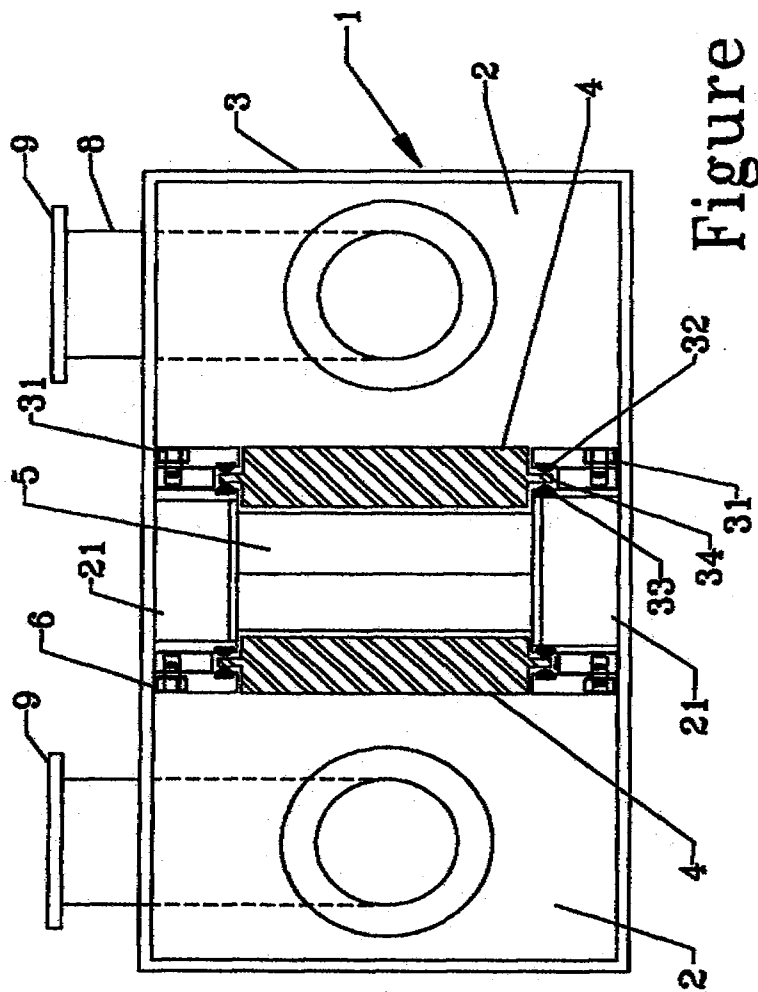


Figure 2

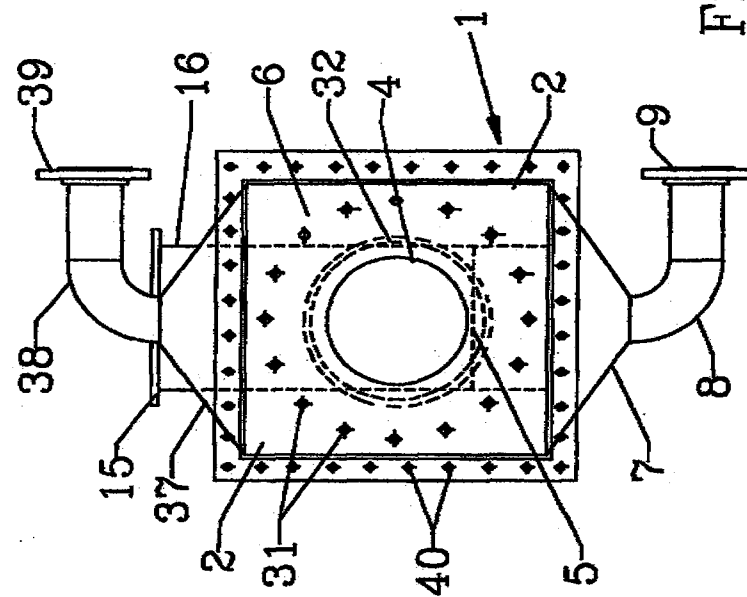


Figure 3

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1 **RADIO FREQUENCY MICROWAVE ENERGY APPLICATOR APPARATUS TO BREAK OIL AND WATER EMULSION**

CROSS REFERENCES TO OTHER APPLICATIONS

This application is a continuation of U.S. application Ser. No. 08/936,063, filed Sep. 23, 1997, now U.S. Pat. No. 5,914,014 and made of reference herein.

BACKGROUND OF THE INVENTION

In the refining industry every attempt is made to extract the maximum usable petrochemical product from the crude oil retrieved from deep within the earth or underseas. It would be fortunate to have a pure sweet product emerge, but this is very seldom the case. More often than not, the crude oil emerges partly as an emulsified mixture of oils, waxes, tars, salt and mineral laden water, fine sands and mineral particulates. Upon storage at the well and refinery sites, some natural settling and stratification occurs, but an intractable emulsion of oil and water and flocculate minerals remains to be dealt with. This waste or slop oil remains as a substantial environmental detriment and represent lost income from recoverable refinery feedstock. Among the many chemical and physical separation techniques, those that act to separate oil molecules from water molecules at their boundary interface with economy serve the oil recovery industry best.

Physical separation techniques employ conductive heating to reduce surface tension at the oil and water boundary interface and centrifuging to separate the less dense oil from water. In those situations in which the oil contains a large number of polar molecules with a hydrophilic (water loving) end and a hydrophobic (water hating) end, reduction of surface tension by direct heating alone will not suffice. And under those conditions in which complex organic compounds increase the density of the oil fraction to nearly that of water, the centrifuge relying on the difference in component densities, will fail to completely separate the components.

Chemical additives used as emulsion breakers often present an economic burden and additional contaminated water disposal problem. In most situations a combination of physical and chemical means are required.

Laboratory and field tests have proven that the application of radio frequency (RF) microwave energy to oil-water emulsions will result in separation at the molecular level to an advantage over other methods. It is believed that the oil-water interface bond is broken as the RF energy agitates the water molecule, a highly polar molecule that spins and twists rapidly in the oscillating radio frequency field. In a similar fashion, the hydrophilic polar end of the oil binding molecules are vibrated most by the radio frequency field. This shearing effect aids in the coalescence of oil droplets separated from the water droplets and the ultimate breaking of the emulsion. The vibration at the polar interface creates localized heating to further aid the separation of the constituents.

The present invention details an apparatus designed to effectively apply microwave radio frequency energy to a pumped stream of hydrocarbon and water emulsion with the maximum absorption of the radio frequency energy in a multimode resonant recirculant microwave cavity. Dual opposing emulsion flow chambers with a centrally supplied microwave waveguide form a double ended resonant chamber with multiple RF energy reflections to effectively treat

the flowing emulsion. The emulsified feedstock enters into the bottoms of both flow chambers and exits from the top having been heated by and treated with microwave radio frequency energy.

DESCRIPTION OF THE PRIOR ART

In U.S. Pat. No. 4,067,683 William J. Klaila teaches a method of electromagnetically heating a high viscosity hydrocarbon fluid for controlling its fluency by using a pyramidal shaped horn composed of a dielectric material that converges inwardly into a oil burner fuel tank. Similar pyramidally and conically shaped radio frequency applicators are directed down a pipe into viscous oil bearing geological structures to heat the oil in situ. This patent, issued in Jan. 10, 1978, makes no claim or reference to the breaking of oil-water emulsions.

Leslie E. Compton, in U.S. Pat. No. 4,174,751 does not use Radio frequency energy to extract "shale oil" in situ. A cursory mention of "electrostatic" method of separation is made in the specification, but is not further elaborated upon. The application of radio frequency energy is not mentioned.

Chahner G. Kirkbride in U.S. Pat. No. 4,279,722 describes improved catalytic reactions in petroleum refining by subjecting the hydrocarbon reactants in contact with catalytic materials to the influence of wave energy in the microwave range. He does not teach a method or apparatus to apply the radio frequency microwave energy. The patent claims improved efficiency in converting hydrocarbons to other hydrocarbons with radio frequency energy in catalytic processes but the radio frequency energy is not used to break emulsions.

In "Microwave Demulsification," C. S. Rang, Bruce K. L. Chang and Peter M. C. Lai, Department of Chemical Engineering, University of Southwestern Louisiana, Lafayette, La., 70504 and W. J. Klaila, Electromagnetic Energy Corporation, Middleboro, Mass., 02346 in the publication Chemical Engineering Comm. 1988, Vol. 73, pp. 227-239, complete some basic laboratory experiments to show that demulsification of oil and water by microwave energy substantially improves separation levels and times. Field tests consisted of directing microwave energy from a 20 KW microwave generator with a cone shaped applicator centered and facing downward in a 10 foot high by 10 foot diameter cylindrical metal tank. The contents of the tank were shown to separate after several hours of radio frequency energy application. This is a batch process, not a flow through process.

Nicolas Wolf, in U.S. Pat. No. 4,582,629 claims a method for enhancing the separation of hydrocarbon and water from an emulsion or dispersion with the application of microwave energy and then heating the emulsion using conventional heating means. Particular means to apply the microwave energy are not described or claimed.

In U.S. Pat. No. 4,810,375, Roger L. Hudgins [and Wolf] et al., treats an oil-water emulsion with a system comprising a microwave energy source and an applicator having an inlet and an outlet for the passage of oil-water emulsion or dispersion without detailed reference to the nature of the microwave applicator. Claims pertain to the use of water separated from the emulsion to flow through and cool a water filled dummy load chamber to absorb reflected microwave energy.

In U.S. Pat. No. 4,853,119, Wolf et al. describes a coalescer medium contained within the microwave applicator to improve the separation of the emulsion components.

In Samardzija U.S. Pat. No. 4,853,507 describes an apparatus for efficient heating of microwave of emulsions or

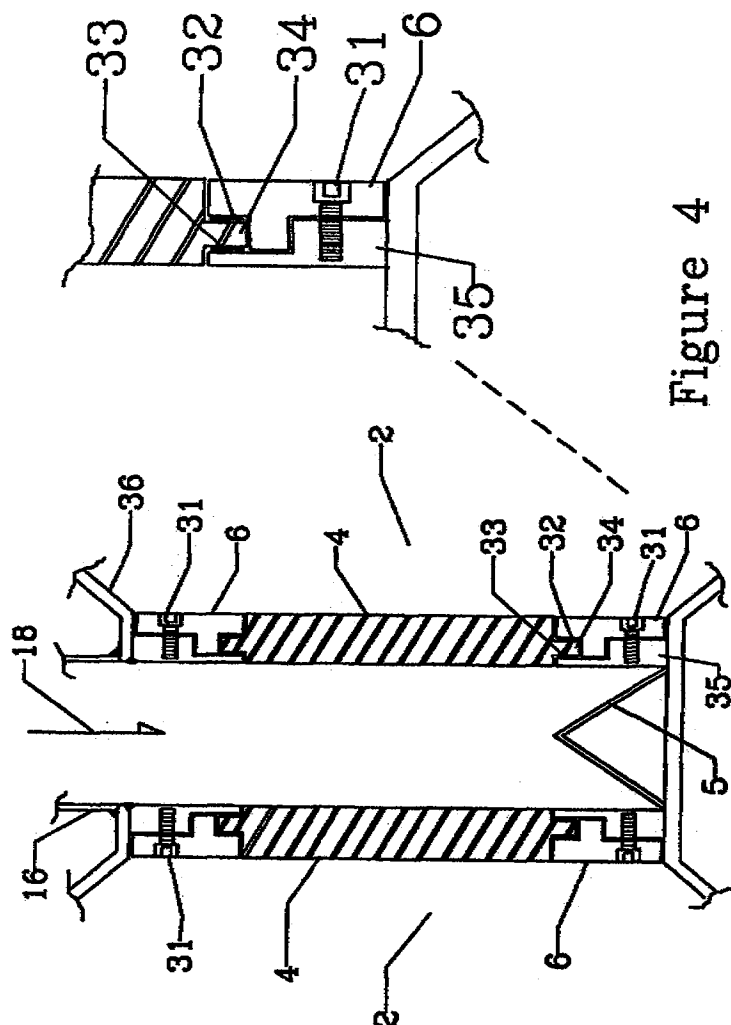


Figure 4

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dispersions having a section of waveguide with a tapered impedance matching membrane formed from low dielectric material to best present impedance matching surface into a liquid filled end of the radio frequency wave guide section. Several other applicator shapes are described in specification and claims for both circular and rectangular waveguides.

In U.S. Pat. No. 4,855,695 Samardzija the microwave energy delivered to the de-emulsifier system is tuned to an optimum voltage standing wave ratio by means of a computerized phase shifter.

Unlike prior art, the preferred embodiment of this invention describes a radio frequency energy applicator that reflects energy into dual opposed radio frequency terminal cavities by means of angled reflector plates located at the terminal end of a rectangular waveguide. Low loss, radio frequency transparent, flat plate windows prevent the intrusion of chemical feedstock into the waveguide. Feedstock flow is upward against gravity to prevent entrained solids from becoming trapped within the resonator cavities. The dual opposed radio frequency terminal cavities act as one multimode resonant microwave cavity to effectively absorb microwave energy. The resonant chamber dimensions closely match the microwave standing wave patterns, given the dielectric nature of the oil and water mixture flowing through the dual opposed cavities.

The waveguide terminal reflector plates are sized and angled to minimize radio frequency losses and to prevent reflected energy from returning to and damaging the radio frequency transmitter. A three port circulator is placed within the transmission path between the transmitter and the microwave applicator to divert any reflected radio frequency to a water cooled dummy load.

In addition, the applicant has made improvements in the method of treating emulsions to aid in their separation and in the apparatus used to apply radio frequency microwave energy to the emulsion feedstock. The inventor recognizes the need first to conventionally preheat the feedstock to melt solids such as waxes and tars to raise their level of dielectric absorption of microwaves prior to treatment with microwaves and to improve feedstock pumping characteristics by lowering viscosity.

The inlet and outlet temperatures are monitored and the flow rate of the feedstock is controlled to maintain optimal dwell time and exit temperature to guarantee the best separation of emulsion components. An optimum temperature differential of the feedstock between the inlets and outlets of the microwave cavities is fed back to the pump feed rate controller. Pumping rate is changed to maintain the proper temperature difference for optimum emulsion breaking. The inventor finds this method preferable over those methods using adjustments in the voltage standing wave ratio (VSWR) to control the feedstock pumping rate.

The inlet is located below outlet to flush out particulate solids such as sand and prevent the trapping of sand and the concomitant loss of flow which leads to overheating of the feedstock.

Particular attention in this design has been paid to preventing stagnation or restriction of flow on the surfaces of the microwave transparent windows. The design of the specific geometry of the treatment chambers prevents hot spots. Hot spots in improperly designed systems result in localized carbonizing of the hydrocarbon feedstock. Conductive carbon buildup on the windows shorts out the microwave field with a catastrophic increase in temperature, resulting in the melting or fracturing of the window material.

Additional protective instrumentation monitors and controls against any flow restrictions in the feedstock path to

prevent against voids and flow stagnation and build up of solids. The microwave transmitter is shut down if any fault condition is detected.

All incoming feedstock is preheated by conventional means, and by hot wastewater separated from treated feedstock, to reduce viscosity and to aid in the prefiltration of rocks and other large solid masses from the feedstock emulsion. The inventor has found that microwave energy couples to the feedstock better at elevated temperature. Feed temperatures of 120 to 180 degrees Fahrenheit or more are needed, depending on the melting temperature of organic solids in the mixture as well as the type and amount of entrained non-melting solids such as dirt and sand.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional elevated view through the microwave applicator and dual processing chambers.

FIG. 2 shows a cross sectional plan view through the microwave applicator and the dual processing chambers.

FIG. 3 shows a elevated face view of a microwave window assembly with one process chamber access cover removed.

FIG. 4 is an elevated cross sectional view of the radio frequency microwave applicator window structure.

DETAILED DESCRIPTION OF THE DRAWINGS

As detailed in FIG. 1, microwave energy 18 is delivered through a hollow waveguide (not shown) which couples to flange 15 of applicator waveguide 16. The microwave energy is divided and deflected to the dual processing chambers by means of angled deflector plate 5. Two plane parallel, microwave transparent windows 4 conduct the microwave energy into dual process chambers 2 constructed of conductive materials. The dimensions of the process chambers are chosen to maximize a multimode resonant pattern at the working radio frequency and feedstock dielectric characteristics. RF frequencies of 915 MHz or 2450 MHz are the frequencies most often used for industrial processing to avoid conflicts with communication devices.

The energy is absorbed by feedstock within the feedstock process chamber space 2 in the form of an oil and water emulsion, enters the chamber through inlet pipe 8 and exits through outlet pipe 38. Flanges 9 couple the inlet pipes to a pumped and if necessary, preheated source of filtered feedstock. Flanges 39 couple outlet pipes to the appropriate feedstock handling equipment such as centrifuges and collection tanks. Metal access covers 3 held in place by fasteners attached around the periphery 40 to provide easy means to inspect and clean process chambers if necessary.

The dual process chambers 2 in combination with deflector plate 5 and window frame 6 form a two lobed, multimode resonant microwave cavity.

In FIG. 2, a cross sectional plan view details the applicator placement within the dual lobed process chamber assembly 1. Looking down into the RF energy waveguide, deflector plate 5 reflects the microwave energy through dual parallel microwave transparent windows 4 into the feedstock flow spaces 2. Multimode resonant microwave patterns between chamber sides 3 evenly treat the feedstock as it enters the process chamber 2 resulting in a fairly uniform distribution of emulsion breaking energy while raising the feedstock temperature evenly throughout the flow volume. Window retaining hardware, in this embodiment of the invention, consist of a series of threaded fasteners 31 holding window frames 6 securely against hollow bulkheads 21 made from

conductive material, such as stainless steel plate. Gaskets 32 and 33 secure the microwave transparent windows 4 against any feedstock leakage into the microwave applicator waveguide. Blind hollow bulkheads 21 serve a structural purpose and restrict the shape of the dual lobed chamber assembly 1 to effective microwave resonance patterns, but do not carry RF energy within the hollow spaces.

FIG. 3 details a face view of one of the plane parallel opposed microwave transparent windows. The feedstock process chamber access cover 3 (not shown) has been removed to show the round window 4 secured in place by window frame 6 with multiple fastening holes 31. Compression gaskets 32 prevent feedstock from leaking into the microwave applicator waveguide 16. Emulsion feedstock enters the treatment space 2 by means of lower pipe 8 with flange 9 and smooth transition 7 and exits feedstock treatment space 2 through smooth transition 37 and pipe 38 with connecting flange 39. Though this drawing shows a round microwave transparent window 4, square and rectangular windows can be used.

A cross sectional view of the radio frequency microwave applicator with attention to a preferred method of mounting the microwave transparent windows is detailed in FIG. 4. Radio frequency microwave energy 18 enters the applicator through waveguide 16 and is reflected by angled deflector 5 through thick TEFLON® or other fluoropolymer microwave transparent windows 4 into dual feedstock reaction chamber spaces 2. The TEFLON® or other high temperature, inert fluoropolymer windows are almost transparent to microwaves, inert and impervious to the feedstock mixture and thick enough to withstand the pumping pressures at the elevated temperatures used to treat the feedstock. Window frame 6 is held in place by recessed mounting hardware 31 presenting a smooth even surface to improve flow characteristics and to prevent entrapment of solids. Compression gaskets 32 and 33 are shown for completeness, although applicant has found that the compression of the tongue of TEFLON® 34 around the periphery of the window between waveguide sidewall 35 and window frame 6 is sufficient. Inner wall 36 of the inlet and outlet transitions to the dual treatment chambers have a smooth surface transition with the window frame 6. Solids, waxes and tars cannot build up and char or carbonize to form radio frequency energy, conductive hot spots that would harm the TEFLON® or other high temperature, inert fluoropolymer windows. In addition, the smooth transition between metal surfaces within the dual treatment chambers reduces the number of unnecessary, electrically reactive protrusions which dissipate or reflect radio frequency energy at microwave frequencies.

The accompanying drawings referred to herein are illustrative of the invention but not restrictive thereto, and, together with the description, serve to explain the principles of the invention.

What is claimed is:

1. Apparatus for breaking an oil and water emulsion feedstock into oil and water streams with a source of radio frequency waves which comprises:

a radio frequency wave guide for receiving radio frequency waves;

a process chamber adjacent the waveguide configured to permit the emulsion feedstock to move therethrough

and to expose the emulsion feedstock to radio frequency waves;

a radio frequency transparent window between the waveguide and process chamber to allow passage of radio frequency energy into the process chamber; and a deflector located in the waveguide oriented to deflect radio frequency waves to the radio frequency transparent window and into the process chamber.

2. The apparatus of claim 1 which also includes a second process chamber adjacent the waveguide and a second radio frequency transparent window between the waveguide and the second process chamber, and a deflector which divides the radio frequency wave and deflects a portion thereof into each of the process chambers.

3. The apparatus of claim 2 wherein the deflector is located at the terminal end of the waveguide between the process chambers.

4. The apparatus of claim 2 wherein the microwave transparent windows are substantially parallel to each other.

5. The apparatus of claim 2 wherein the waveguide terminal reflector plates are sized and angled to minimize radio frequency losses and to prevent reflected energy from returning to a source of the radio frequency energy.

6. The apparatus of claim 1 wherein the radio frequency transparent window is made of a fluoropolymer.

7. A system for breaking oil and water emulsion feedstock using radio frequency energy which comprises:

a source of radio frequency energy;

a waveguide for conveying the energy for use to treat the emulsion feedstock;

a feedstock process chamber having at least one inlet and at least one outlet oriented adjacent the waveguide;

a radio frequency transparent window between the process chamber and the waveguide to allow passage of radio frequency energy from the waveguide into the process chamber;

a deflector of radio frequency energy oriented in the waveguide to direct the radio frequency energy from the waveguide through the window and into the process chamber; and

a pump for passing the emulsion feedstock through at variable rates responsive to the temperature rise of the emulsion feedstock as it passes through the process chamber receiving radio frequency.

8. The system of claim 7 which also includes a second process chamber adjacent the waveguide and a second radio frequency transparent window between the waveguide and the second process chamber, and a deflector which divides the radio frequency wave and deflects a portion thereof into each process chamber.

9. The system of claim 8 wherein the deflector is located at the terminal end of the waveguide between the process chambers.

10. The system of claim 8 wherein the microwave transparent windows are substantially parallel to each other.

11. The system of claim 8 wherein the waveguide terminal reflector plates are sized and angled to minimize radio frequency losses and to prevent reflected energy from returning to a source of the radio frequency energy.

12. The system of claim 7 wherein the radio frequency transparent window is made of a fluoropolymer.

* * * * *

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United States Patent

[11] 3,616,375

[72] Inventor: Kiyoshi Inoue
100 Sakata Kawasaki, Kanagawa, Tokyo,
Japan
[21] Appl. No. 613,791
[22] Filed Feb. 3, 1967
[45] Patented Oct. 26, 1971
[32] Priority Mar. 3, 1966
[33] Japan
[31] 41/12943

[54] METHOD EMPLOYING WAVE ENERGY FOR THE
EXTRACTION OF SULFUR FROM PETROLEUM
AND THE LIKE

[52] U.S. Cl. 204/162 B,
204/162 S, 204/168

[51] Int. Cl. B01J 1/10,
B01J 1/12

[50] Field of Search 162 AE, 162 S, 163, 193

[56] References Cited

UNITED STATES PATENTS
1,897,617 2/1933 Mehlre 204/162
2,578,377 12/1951 Smith 204/162 (S) X

ABSTRACT: A method of decreasing the sulfur content of crude oil and other petroleum products to which the sulfur is present in an elemental state or in chemical combination with an organic substance (i.e., the crude oil), in which high-energy radiation at relatively low temperatures ruptures carbon-sulfur bonds in the form of H_2S or carbon-sulfur bonds as CS_2 , etc., so that gaseous sulfur-containing compounds are evolved from the liquid. The periodic high energy can be an impulsive spark discharge or accompanied by vibrational shock of sonic or ultrasonic frequency for activating with or without bonds to produce gaseous sulfur-containing compounds is also suitable. The apparatus includes an activation chamber through which the crude oil is pumped while being transported around a tank or the like means for recovering or discharging the gases, and one or more sulfur-recovering devices such as a spark-discharge electrode, condensation generator, ultrasonic or sonic transducer, shock wave generator, high frequency electrode assembly, laser or microwave generator.

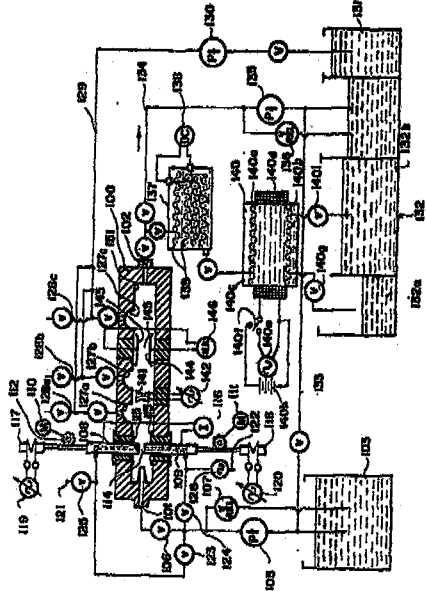


FIG. 1

SHEET 1 OF 6

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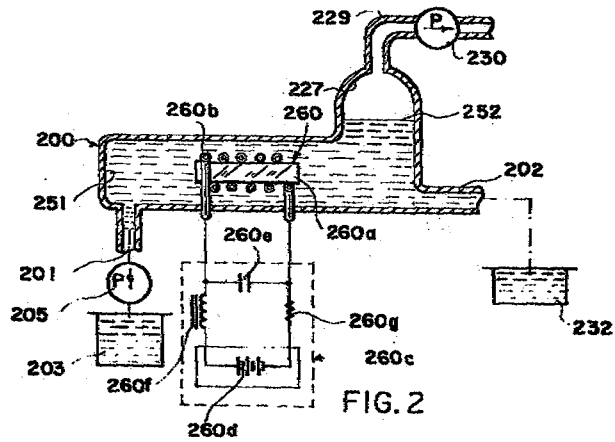


FIG. 2

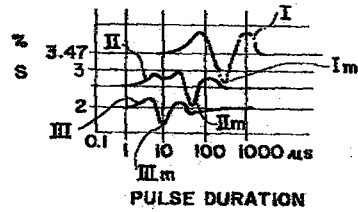


FIG. 11a

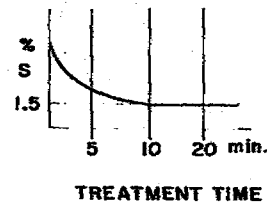


FIG. 11b

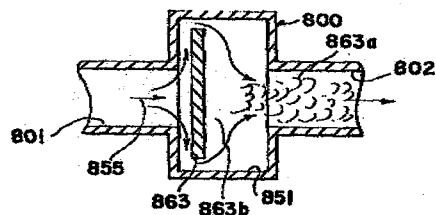


FIG. 8

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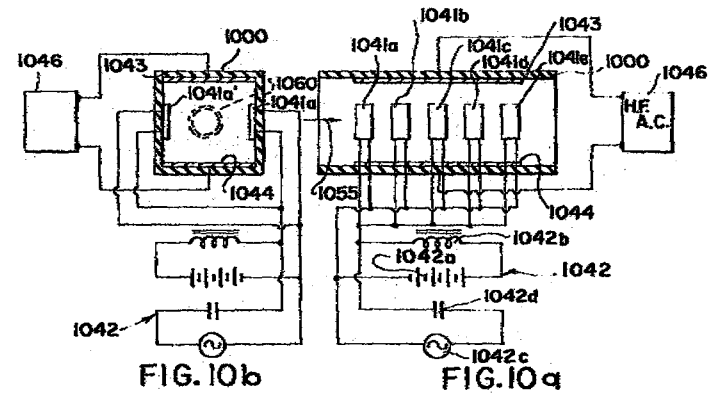


FIG. 10b

FIG. 10a

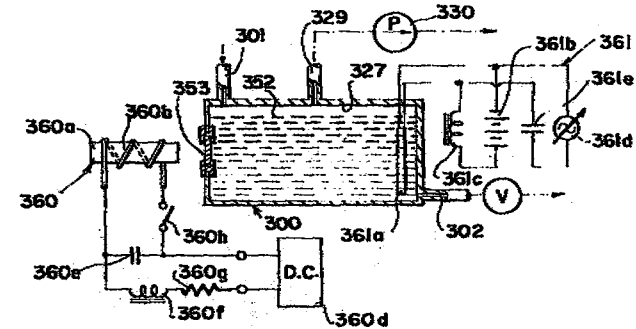


FIG. 3

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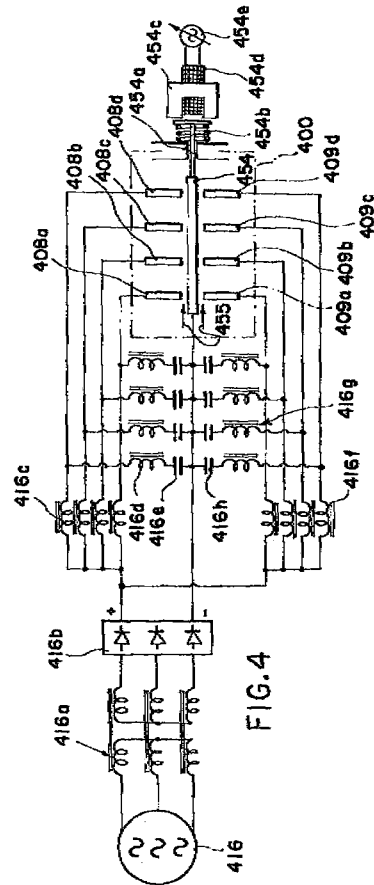


FIG. 4

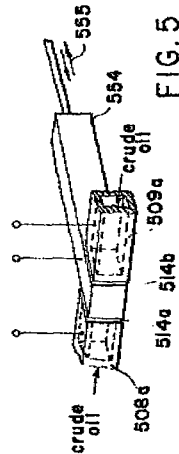


FIG. 5

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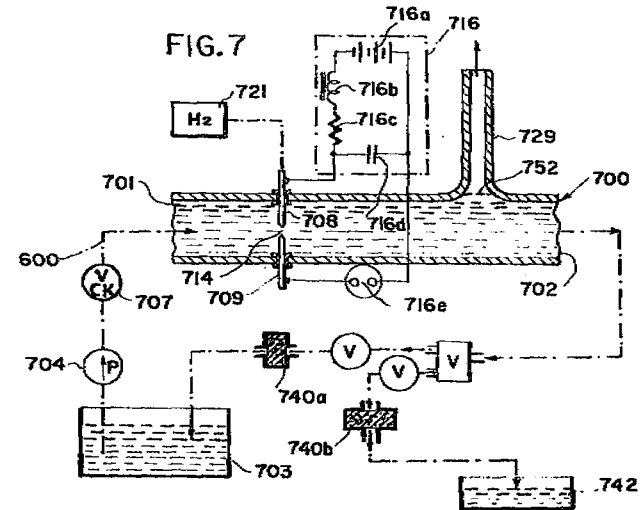


FIG. 7

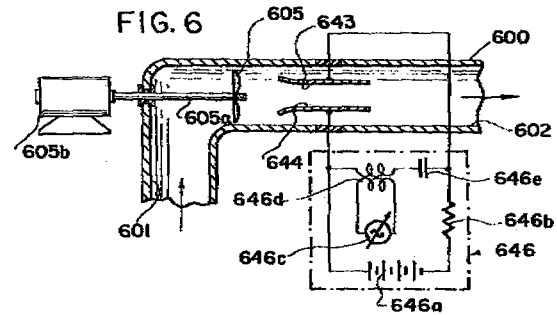


FIG. 6

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METHOD EMPLOYING WAVE ENERGY FOR THE
EXTRACTION OF SULFUR FROM PETROLEUM AND
THE LIKE

The present invention relates to a method of and apparatus for the extraction of sulfur from petroleum and the like and, more particularly, to the diminution of the sulfur content in organic liquids in which the sulfur is present in an elemental state as a sulfur bridge between organic molecules or in simpler chemical combinations (e.g., as mercaptans).

The presence of sulfur in chemically combined or elemental form in crude oil and other liquid petroleum products has posed significant problems in terms of air pollution and detrimental to health. Frequently, the compounds of industrial plants, power plants, heating installations and the like require fuel oils of relatively low grade and subject it to minimum refining. When the crude oil from which the fuel is derived contains a large proportion of sulfur, it is found that combustion of the fuel releases into the atmosphere noxious gases including hydrogen sulfide (H₂S), sulfur dioxide (SO₂) and sulfur trioxide (SO₃). The sulfur oxides are among the most dangerous components of air pollution with respect to the health of the population and are detrimental in a technological sense as well, inasmuch as they are hydrolyzed to sulfurous and sulfuric acids and may form corrosive acids by combination with ambient moisture.

While many systems have been proposed heretofore for the reduction of the sulfur content of fuel oils and crude oils, these systems have proved uneconomical for the most part. Thus, mere vacuum treatment of crude oils is ineffective for significantly reducing the proportion of sulfur in the organic liquid, while thermal treatments are expensive and must be carried out extensively, severely modify the composition of the oil. As a practical matter it has not heretofore been economically feasible to treat crude oils, fuel oils and like organic sulfur-containing liquids, economically, efficiently, in large volume and at low cost.

It is, therefore, the principal object of the present invention to provide a system for reducing the sulfur content of organic liquids and, especially of crude oils and petroleum products, whereby the aforementioned disadvantages can be avoided and desulfurization effected economically and efficiently.

Another object of this invention is to provide an improved method for the desulfurization of petroleum liquids which may be carried out conveniently without substantial capital expenditure, is effective to reduce the sulfur content to surprisingly low levels, and is relatively simple and convenient.

Still another object of my invention is to provide an improved apparatus for the desulfurization of crude oils and the like.

These objects and others which will become apparent hereinafter are attained, in accordance with the present invention, by a system for the desulfurization of crude oil and other petroleum liquids containing sulfur in a free or chemically combined state, which is based upon my surprising discovery that certain high-energy (radiant or vibrational) sources may be used to treat the sulfur-containing liquid without substantial heating thereof, but yet are capable of rupturing and reforming chemical bonds involving the sulfur so that a substantial proportion of the sulfur is reformed into compounds such as hydrogen sulfide, carbon disulfide, etc., which are gaseous at ambient temperatures and are readily evolved from the liquid.

While I do not wish to be bound by any theory in this regard, it appears that several free-radical-type reactions may be involved in that the release of sulfur from organic compounds to which it is chemically bound preferentially results in the formation of gaseous compounds mentioned above. Thus, it is conceivable that compounds having carbon-sulfur bonds may be broken between the carbon and sulfur to form an active or activated sulfur atom which, because of its proximity to large numbers of hydrogen atoms (some of which may be released from the organic molecule by the high-energy activation field), forms with these hydrogen atoms or with hydrogen

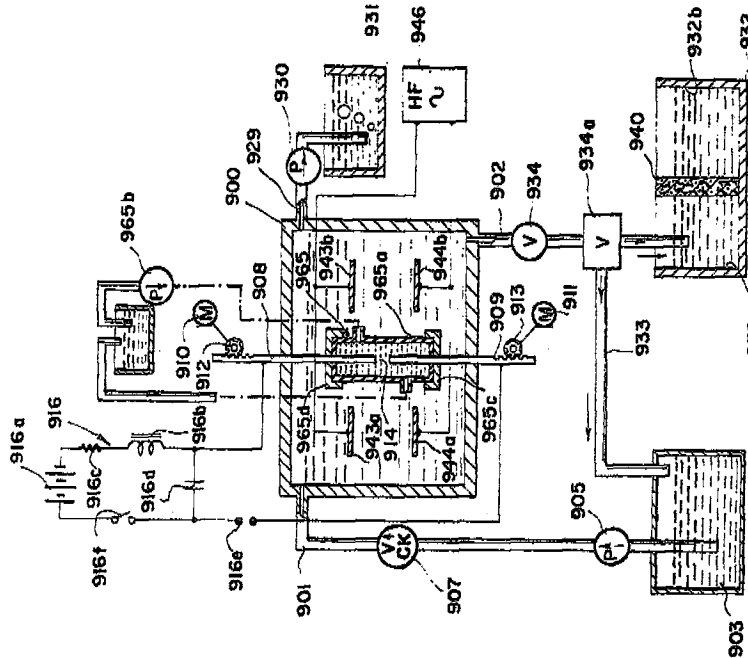


FIG. 9

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atoms stripped by the sulfur from the molecule, highly volatile hydrogen sulfide. The latter is only limitedly soluble in the liquid and thus emerges therefrom in the form of gas bubbles. Similarly, the sulfur atom may attack a carbon atom in the organic chain to eventually produce carbon disulfide. Another possible mechanism for the formation of this volatile sulfur-containing compound is the rupture, at the high energy referred to, of a carbon-carbon bond adjacent to a carbon-sulfur bond. In this case, an activated C-S* species may release a further sulfur atom in a chemically bonded state or combined with a free sulfur atom to form carbon disulfide.

According to a further feature of this invention, the period pressure of the vehicle sulfur-containing compounds above a free surface of the liquid treated is reduced by floating this surface with a gas stream free from the sulfur-containing gases, hydrogen sulfide and carbon disulfide or by evacuating the space above the free liquid surface to draw the evolved gases therefrom.

According to one aspect of this invention, the high-energy activation of the sulfur-containing crude oil is effected by an impulsive electric discharge across a pair of electrodes between which the liquid flows. The electrodes may, moreover, be composed of substances which catalyze the desulfurization act and I have found, for example, that electrodes composed of alloys containing tungsten, molybdenum, vanadium, titanium, chromium, cadmium and rhodium or in combination, have catalytic effects. The electrodes may have these alloying components incorporated in lead or copper and copper/iron alloy less metals. In spite of the use of high-energy discharge, it has been found to be possible to keep the heating of the liquid at a minimum so that the reaction effectively takes place at ambient temperature or pressure.

As will be apparent hereinafter, spark-type discharges have the advantage that they not only provide the electrostatic energy and the characteristic of sonic or supersonic transients. Thus, for example, it has been found that sonic vibrations alone or in combination with some other high-energy or high-frequency activation, can activate the crude oil for the desulfurization reaction. An impulsive spark discharge within the liquid at a sonic frequency has the characteristics of an electroacoustic transducer inasmuch as it applies a shock wave to the liquid at the sonic frequency.

According to another aspect of this invention, the high-energy source is a laser which appears to activate the desulfurization reaction by photochemical means. The laser effect is indeed surprising in view of the fact that efforts to photochemically desulfurize crude oil have little effect when conventional techniques are employed. The laser may, moreover, be disposed within the liquid-containing vessel so that there is minimal loss of laser energy. Microwave energization of the liquid also has been found to be effective preferably in conjunction with one or more of the other modes of activation described herein.

Activation may, as indicated earlier, result from sonic or shock generators disposed in the liquid or in force-transmitting relationship therewith. Thus, for example, a spark discharge in the liquid itself may serve to generate shock or sonic waves, although it is also possible, according to this invention, to effect a spark-discharge in a relatively inactive liquid separated from the liquid under treatment by a flexible membrane or the like. In my copending application Ser. No. 308,487 filed 18 Nov. 1965 (now U.S. Pat. 3,512,384) as a continuation-in-part of my application Ser. No. 41,080, Ser. No. 329,195, and Ser. No. 104,758 now U.S. Pat. Nos. 3,232,085, No. 3,232,086 and No. 3,208,254, I have described shock wave generators of this type. In such generators, one or a series of discharges may be effected in a liquid medium in a substantially closed chamber at least one wall of which is flexible or movable for transmitting the shock to some other medium. Other electroacoustic transducers may, of course, also be employed. I have found that frequencies in the kilocycle and megacycle range (i.e., from 1 kc. to 100 mc./second and preferably from 50 kc./second to 10

13 (second) are most effective using transducers of this character. The transducer may be piezoelectric systems having vibrational elements immersed in the liquid for applying the vibrations thereto. Thus, magnetostrictive devices are also suitable for the purposes of the present invention.

In any application of the present invention, the apparatus of FIG. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000.

5 connected in shunt across the pump 105 to return excess oil to the tank 103. The desulfurization reaction is here induced in part by spark discharge, in part by ultrasonic vibration and in part by a high-frequency electrostatic field as will become apparent hereinafter. It will be understood, however, that while it is preferred to use ultrasonic vibration and electrostatic field reversal concurrently with spark discharge, it is also possible to induce desulfurization without such joint action. At the first stage, the vessel 100 is provided with a pair of electrodes 108, 109 which may be tubular and can be composed of a catalytic electrolyte substance as set forth in the specific examples below. Using motors 110 and 111, connected via rack-and-pinion drives 112 and 113 with the electrodes 108 and 109, respectively, spark discharge at a substantially constant gap is effected across the gap 114 in spite of erosion of the electrodes. The electrodes 108 and 109 are guided for movement toward and away from one another in electrically insulating sleeves 115, while being energized by an inductive-discharge source (e.g., a relaxation-type oscillator or charge-discharge capacitor) 116. Vibrations are imparted to the electrodes 108 and 109 in their major dimension via magnetostrictive coils 117, 118 whose coils, in turn, are energized by ultrasonic or sonic-frequency alternating current sources 119 and 120.

It has been found to be advantageous, if hydrogen sulfide is the most desired gaseous sulfur-containing component, to supply hydrogen to the region of the gap 114 although this is by no means essential. Hydrogen can be fed to the gap in the apparatus of FIG. 1 via hydrogen inlets 121 and 122 when the valves 123 and 124 of the oil supply line are closed. In the event it is desired not to deliver hydrogen to the gap 114, it is preferred, according to a feature of this invention, to feed the oil to be desulfurized as a coolant or to induce turbulence through the tubular electrodes 108 and 109. For this purpose, valves 125 and 126 of the hydrogen-supply lines are closed, and valves 123 and 124 are open. Valve 106 can be wholly or partially closed at the same time.

At a number of collection sources along the vessel 100, 1 provide collection domes 127a, 127b and 127c in which a gas pressure equal to that of the liquid pressure is sustained. In each of these domes 127a-127c, a free surface of the crude oil is exposed and sulfur-containing gases are evolved. These gases are withdrawn via simple lines 128a, 128b and 128c, respectively, when tests of the volume of evolution and composition of the evolved gas are desirable. Normally, however, the evolved gases are collected in a line 129 and conveyed via a pump 130 whose suction pressure determines the pressure in the domes, to a washing station 131, represented only diagrammatically but constituted by any conventional scrubbing-tower, condenser arrangement or the like capable of removing the noxious sulfur-containing substances. When absorption columns are employed for this purpose, the sulfur-containing components can be recovered.

When it is desired to continuously circulate the crude oil, as in the case with crude-oil treatment upon tanks or the like, in which, for example, the reactor 103 may represent one of the built tanks of a ship and tanks 132 represent other bulk tanks in which crude oil of various degrees of purification are collected, a line 133 is provided between the outlet line 134 and the inlet side of pump 105. A further pump 135 and a respective relief valve 136 are used when reversal of the flow direction is desired. It has been found to be highly advantageous to pass the oil through a conventional electrostatic filter 137 which is energized with a high-voltage DC current from a source 138. The oppositely charged electrodes 139 collect particulate materials as the liquid flows therethrough. It has also been found to be desirable to provide a magnetic filter 140 in the outlet line, such filter being of the type described and claimed in my copending application Ser. No. 598,512, filed 1 Dec. 1966.

In this type of filter, a mass of permanently magnetic or magnetically permeable particles is coalesced under a pair of sources 140a and 140b and tend to coalesce under the later particle magnetic forces to form relatively constricted

Another feature of this aspect of the invention resides in disposing ultrasonic transducers along the walls of the vessel and energizing them via respective tuned circuits or other means for vibration at a number of characteristic frequencies constituting harmonics of one of the characteristic frequencies of the carbon sulfur bond under test. In any copending applications Ser. No. 399,243 filed 25 Sept. 1964 (now U.S. Pat. 3,446,718) and Ser. No. 356,715 of 2 Apr. 1964, (now U.S. Pat. 3,330,746) I have described how rupture of a chemical bond can be facilitated with little heating of the reaction mass when the frequency of vibration of the transducer is a harmonic or the principal characteristic frequency of the partition bar bellows. All of this related disclosure is incorporated herein by reference. In more general terms, it can be said that the frequency of the ultrasonic vibration should be

$$f = (1/2\pi) \sqrt{k/m} \quad (1)$$

where k is the elastic constant and m is the thermal conductivity of the molecule. When reference is made to integral harmonics, it is to be understood that the integral subharmonics frequently are effective for the present purposes.

I have also observed that desulfurization of the gas can be facilitated by the application thereto of a high-frequency electrostatic field even though this field is of insufficient magnitude to produce a corona discharge breakdown across the dielectric gap. To this end, a pair of electrodes are spaced apart in the vessel and extend parallel to the direction of liquid flow and are energized at the principal frequency f indicated above or the sub- or superharmonics thereof.

Yet another feature of the apparatus of the invention resides in the provision of an inlet-outlet means within the vessel alone or in combination with the other high-energy sources described above. The shock-tube means may include a liquid-exiting nozzle having flexible walls and within which a spark discharge is developed as described in U.S. Pat. Nos. 3,232,085, No. 3,232,086 and No. 3,208,254, or depending application Ser. No. 507,487 mentioned earlier.

The above and other objects, features and advantages of the present invention will become more readily apparent from the following description, reference being made to the accompanying drawing in which:

FIG. 1 is an axial cross-sectional view diagrammatically illustrating an apparatus for carrying out the present method in accordance with this invention making use of linear energy;

FIG. 2 is another diagram in cross section showing a vertical plane showing the use of a laser for the desulfurization of the fuel oil;

FIG. 3 is a circuit diagram of a system using electric discharge for the desulfurization;

FIG. 4 is a perspective view illustrating some manifolds of the system of FIG. 1;

FIG. 5 is an axial cross-sectional view of a system using cavitation effects in conjunction with high-voltage fields for the removal of sulfur from crude oil;

FIG. 6 is a similar view of another system making use of cavitation phenomena;

FIG. 7 is an axial cross-sectional view of a cavitation inducing means adapted to be employed with the system of FIG. 7;

FIG. 8 is a vertical cross-sectional view through the apparatus operating in accordance with the principles of this invention and making use of shock waves to induce the desulfurization reaction;

FIGS. 10a and 10b are cross-sectional views through another treatment vessel in accordance with this invention;

FIGS. 11a and 11b are graphs illustrating the invention.

In FIG. 1, 1 shows a desulfurization vessel 100 having an inlet 101 and an outlet 102 at the opposite axial ends of this generally elongated vessel for the desulfurization of sulfur-containing crude oil. A continuous flow of crude oil is drawn from a tank 103 and delivered by a pump 105 and a valve 106 to the inlet 101, a pressure-release bypass valve 107 being

in accordance with a more specific feature of this invention, a pair of electrodes are juxtaposed in the liquid stream in this treatment chamber and are energized with a discharge energy of 50 to 1,000 joules per discharge at a rate of substantially 5 to 500 pulses per second. Under these circumstances, the impulsive character of the discharge and the cavitation produced by collapse of the expanding discharge region reduces the rupture of the sulfur bond and reforms the sulfur into volatile gases.

According to a further feature of the invention, the high-energy activating stream includes a laser surrounded by a pumping lamp 170 to heat the vessel through which the fuel oil is circulated. In this case, the laser being exposed externally to the vessel, it is, however, desirable to conserve the laser energy by directing the laser directly within the vessel so that even indirect reflection of an effective wavelength performs a desulfurization function. Similarly, a microwave source can be disposed externally of the vessel with waveguides of appropriate character connecting the microwave cavity with the vessel through a window transparent to microwave energy.

passages. The vessel 100 is surrounded by a magnetic coil 140 which may be energized by an AC source 140a via a switch 140b. When so energized, the coil 140a applies a rapidly alternating field to the particles and thus dislodges connected material. Concurrently with the energization of coil 140b by the source 140a, valve 140g is open to collect contained fluid in the treatment chamber 132a. While, when the alternating magnetic field is terminated or a DC magnetic field from battery 140b is applied to the coil 140a to reactivate the passages, the valve 140g is open and purified crude oil is collected in compartment 132b of the tank 132.

Downstream of the spark at 114, I provide a magnetostrictive electronic transducer 141 adapted to apply high-frequency vibrations to the liquid within the vessel 100. The magnetostrictive vibrator 141 is energized by a high-frequency oscillator 142. Further downstream, a pair of electrodes 143 and 144 are juxtaposed with a relatively wide gap 145 and extend parallel to the direction of flow of the oil. A high-frequency high-voltage oscillator 146, capable of generating high-power radio-frequency waves, is connected across the plates 143 and 144 so that a high-frequency field is applied in the 10^6 to 10^8 mc. range across the dielectric liquid.

In operation, a crude oil may be delivered to the tanks 103 of a transport vessel such as a seagoing tanker and transported to a local source from the sources for refining and distribution. Alternatively, refining may be carried out at the source of the crude oil and a heavy oil containing considerable sulfur may be transported by the vessel. In either case, during the transport of the crude oil, the oil is circulated by a pump 105 in the desulfurization chamber 109 and the line 133 through the compartment 141 along a plurality of successive treatment stages. In the first treatment stage, a spark discharge is effected between the aluminum, copper or from electrodes 108, 109 containing tungsten, molybdenum, thallium, vanadium, cerium, cerium or zinc alloying metals to catalyze early desulfurization.

Spark excitation frequencies in the kilocycle or megacycle per second range are carried out. The vibration imparted to the electrodes 108 and 109 may be at the same frequency as the discharge source 146 or at a different frequency (preferably 5 to 400 pulses per second) as induced by the vibrations 117, 119 and 118, 120. The evolved sulfur-containing gases, primarily hydrogen sulfide and carbon disulfide, are collected in the domes 127a along with quantities of hydrogen, methane and alkanes having carbon numbers up to about 6. The gaseous hydrocarbons can be separated by condensation at 131 and the sulfur-containing gases collected by absorption and converted to useful products or discarded.

The oil then is activated by the magnetostrictive vibrator 141 with sonic or ultrasonic frequencies, the released gases being collected in zone 127b and being treated or separated in the manner described.

Finally, the crude oil passes through a high-frequency treatment zone between the plates 143 and 144 where radiofrequency activation with corona discharge or without such discharge releases further quantities of the sulfur-containing gas. After passage of the oil several times through the treatment vessel, it is found that the major part of the sulfur is removed and the thus purified oil is passed through the electrostatic filter 137 (at which electrically charged or polar substances are removed) and then through the magnetic filter 140 which traps minute particles. The purified crude oil is collected in compartment 132b.

In FIG. 2, I show a modified system for the desulfurization of a crude or semi-refined oil adapted to be used on shipboard, in a preliminary treatment stage of an oil refinery or between the oil well and the storage tank in an oil producing field. In this embodiment, the treatment vessel 200 is supplied with the crude oil at its inlet 201 by a pump 203 from a crude oil source 203; the latter may be a tank of the oil-refinery complex, the well or a storage tank at a refinery. The vessel 200 forms a treatment chamber 251 in which a high-energy and high-frequency source represented at 260, is disposed. The high-

The shock generator 945 was filled with kerosene with continuous circulation and a single discharge of an energy of 7,000 joules was carried out between aluminum electrodes containing 2 percent by weight vanadium. 55 cc. of the heavy oil were thus treated and 22 cc. of hydrogen sulfide were evolved together with traces of carbon disulfide, sulfur dioxide and carbon dioxide. Analysis showed that the sulfur content was reduced by about 1/3, to a maximum of 2 percent by weight.

EXAMPLE III

Using again the system of FIG. 9 and the impulsive source of example II, desulfurization was promoted by high-frequency energization of the electrodes 943a, 944a, and 945a. Each of the electrodes was rectangular with overall dimensions of 2x2 mm. and interelectrode gaps of 10 mm. A peak potential of 1,200 volts and of a square-wave form at 1,000 kc./sec. was applied between the electrodes and a corona discharge was observed. Analysis in the same treatment time showed that 2.25 percent by weight of sulfur was removed, a net removal of approximately 75 percent of the original sulfur. When the impulses of the shock generator 945 and the field of the electrodes 943a, 944a, 945a were applied separately, the total sulfur removal was less than that obtained when both types of activation were carried out simultaneously. The synergistic results have not been fully ascertained.

EXAMPLE IV

Using a system of the type illustrated in FIG. 1, a crude oil containing 2.5 to 3.0 percent by weight of sulfur was processed at a flow rate of 7 to 8 liters/minute, the vessel 108 having a length of about 150 mm. and a generally rectangular cross section of 40x50 mm. The electrodes 106 and 109 had a diameter of about 2.5 mm. and were composed of copper. With a mean voltage of 40 volts, a mean current of 5 amp. and a spark repetition frequency of 100 kc./second, 900 to 1,600 cc./minute of gas was evolved, the gas containing 1.2 percent hydrogen sulfide, 45.5 percent hydrogen (represented as C_2H_4), 25 percent hydrogen and 11 percent methane. At 35 volts (mean voltage) and 4 amp. mean current at 103 kc./second repetition frequency, 800 to 1,400 cc./minute of gas were evolved containing 3.4 percent hydrogen sulfide. At approximately 1 amp./second, a mean voltage of 50 v., a mean current of 3 amperes, and a gas evolution rate of 350 cc./minute, a somewhat lower hydrogen sulfide proportion was obtained. As a rule, maximum efficiency was found with spark repetition frequencies between 80 kc./second and 1 mc./second.

EXAMPLE V

The apparatus of FIG. 1 was employed to determine the catalytic effect of the electrode material upon the gas-evolution rate and the proportion of hydrogen sulfide combined within the evolved gases. The vessel having the dimensions given in example IV was employed with five pairs of spaced-apart electrodes (electrode diameter and flow rate as given in example IV) with a mean current of 5 amp. and a mean voltage of 46 volts. The crude oil, originally at a temperature of about 50° C. showed no increase in temperature. Using spark discharge at about 100 kc./second, the copper electrodes produced 2,800 cc./minute of gas and 0.2 percent H_2S therein. When the electrodes were replaced by catalytically effective electrodes of the following composition, the gas evolution rate was raised to 3,100 cc./minute and the H_2S proportion to 4.6 percent. By contrast, the use of electrodes of the same basic metal as those of the catalyzed electrodes but without the catalytically effective oxide produced 3,510 cc./minute of gas with, however, a hydrogen sulfide content of only 0.3 percent. With an iron-on-sulfide catalyzed electrode serving as the positive electrode in each of the pairs and catalyzed copper, aluminum, nickel, chromium and zinc electrodes

trodes serving as the negative electrode of each of the five pairs, the gas evolution rate became 2,500 cc./minute and the H_2S proportion increased to 5.5 percent.

Catalyzed electrodes

	5% by weight	AlO ₃	balance aluminum
Nickel	1% by weight	NO	balance nickel
Chromium	1% by weight	Cr ₂ O ₃	balance chromium
Copper	1% by weight	Cu ₂ O	balance copper
Zinc	1% by weight	ZnO	balance zinc
Iron	5% by weight	Fe ₂ O ₃	balance iron

When tungsten, molybdenum and titanium were incorporated in these base metals or in the corresponding oxides in the oxides, similar catalytic results were obtained. In fact, excellent results were achieved with 2 percent by weight vanadium oxide in aluminum, copper or iron.

EXAMPLE VI

Desulfurization was carried out upon 5 liters of Kadaji crude oil containing 3.7 percent by weight sulfur using the electrode setup of example IV. During the first run, a mean voltage of 50 volts and a mean current of 3 amperes was employed with electrodes of 2.5 mm. in diameter. The graph of FIG. 11a illustrates three successive runs and the desulfurization characteristics of each run. It was observed that, when the sulfur content is plotted against the pulse duration of the discharge (see curve 1), the sulfur content initially rises slightly, then falls sharply to a minimum L, and then again comes to a peak. The increase in sulfur content appears to be a consequence of the recombination of released free sulfur into chemically bonded sulfur. Consequently, in this example, the pulse duration was gradually increased until the minimum L, was attained at approximately 200 microseconds. At this point, the discharge was cut off and the pulse duration reset at about 20 microseconds corresponding to the trough L, of the curve 11. Initially was about 2.4 percent by weight, the sulfur content out with a pulse duration of the second run was reduced to approximately 2 percent by weight. The third run was carried out with a pulse duration of 100 microseconds (FIG. 11b) during the third run (graph 11b) and terminated when the sulfur content fell to about 1.5 percent by weight. As shown by the graph of FIG. 11b, at each run the sulfur content leveled off after about 10 minutes of treatment time. Thus each run was continued for about 10 minutes and the total treatment time was 30 minutes for the three runs. It was found that ultrasonic vibration, at about 460 kc./second, using the system illustrated in FIGS. 11a and 11b with electrode energies of 15 watt/cm² of transducer surface, effectively reduced the sulfur content of 5 percent sulfur crude oil to 2 percent by weight. When ultrasonic radiation of this frequency was employed in the system of FIG. 1 (Examples IV-VI), the increased rate of sulfur removal and the degree of sulfur removal exceeded substantially the total which would be expected from spark discharge and ultrasonic vibration alone.

The invention described and illustrated is believed to admit of many modifications within the ability of persons skilled in the art, all such modifications being considered within the spirit and scope of the appended claims.

1. A method of desulfurizing a petroleum liquid such as a crude oil or a feed oil containing organic molecules having at least some chemically bound sulfur, comprising the steps of subjecting the catalyst-free liquid to wave energy in the range of kilocycles/second to megacycles/second without substantial increase of the temperature of said liquid and of a frequency, intensity and duration capable of releasing at least part of the chemically bound sulfur from said liquid by converting it to sulfur-containing gases, and separating the sulfur-containing gases thus formed from said liquid, said wave energy being

derived from at least one energy source from the class of spark discharge, shock wave mechanical vibration, laser and microwave sources.

2. The method defined in claim 1 wherein said liquid is passed continuously through a treatment chamber in which the liquid is subjected to said wave energy and the separation of said sulfur-containing gases is effected at least in part by applying a return pressure to said liquid and collecting sulfur-containing gases above a free surface of the liquid upon its subjection to said wave energy.

3. The method defined in claim 1 wherein said liquid is continuously recirculated through said chamber until the sulfur content of said liquid drops below a predetermined level.

4. The method defined in claim 3, further comprising the step of reducing the release of sulfur-containing gases from said liquid during the continuous displacement of said liquid by creating cavitation in the moving liquid.

5. The method defined in claim 3 wherein said wave energy is at least partially produced by subjecting the liquid to a laser beam or a wavelength adapted to activate the separation of sulfur from said liquid.

6. The method defined in claim 5, comprising the step of forming a laser in said liquid to subject the latter to said beam.

7. The method defined in claim 3 wherein said wave energy is at least in part produced by effecting an electric discharge in said liquid.

8. The method defined in claim 7 wherein said electric discharge is an impulsive spark discharge generated periodically across a pair of spaced-apart electrodes at a frequency in the kc./sec. and mc./second range.

9. The method defined in claim 8, further comprising the step of catalyzing the release of sulfur from said liquid by contacting it with a catalytically effective quantity of a substance selected from the group which consists of tungsten, molybdenum, titanium, vanadium, chromium, chromium or zinc and oxides or salts thereof and incorporated in at least one of said electrodes.

10. The method defined in claim 3 wherein said wave energy is applied to said liquid in part by passing same between a pair of spaced-apart plates and applying a relatively high periodic electrostatic potential across said plates at a frequency in the kilocycle or megacycle range.

11. The method defined in claim 3 wherein said wave energy is applied to said liquid at least in part by subjecting same to a shock wave from a shock-wave generator immersed in said liquid.

12. The method defined in claim 11 wherein said shock wave generator includes a vessel filled with a force-transmitting liquid and separated from the sulfur-containing liquid by a flexible wall, further comprising the step of generating an electric discharge in the liquid within said vessel to generate the shock wave.

13. The method defined in claim 3 wherein said wave energy is applied to said liquid at least in part by immersing in said liquid an electroacoustic transducer, further comprising the step of energizing said transducer at sonic or ultrasonic frequency capable of promoting the release of sulfur from said liquid.

14. A method of desulfurizing crude oil or fuel oil containing molecules having at least some chemically bound sulfur, comprising the steps of circulating the oil continuously through a treatment zone, in the form of a catalyst-free liquid at ambient temperature; subjecting said liquid in said zone to at least one of the following forms of wave energy of a frequency, intensity and duration sufficient to release at least part of the chemically bound sulfur from said liquid, thereby converting the released sulfur to sulfur-containing gases, said forms of wave energy consisting of laser energy, vibrational and shock wave energy of a frequency in the range of kilocycles or megacycles/second and electroacoustic energy in the range of kilocycles and megacycles/second; collecting above the liquid in said zone the sulfur-containing gases released from said liquid; and evacuating said sulfur-containing gases from said zone.

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United States Patent [19]
Wolf

[11] Patent Number: **4,582,629**
 [45] Date of Patent: **Apr. 15, 1986**

[54] **USE OF MICROWAVE RADIATION IN SEPARATING EMULSIONS AND DISPERSIONS OF HYDROCARBONS AND WATER**

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[73] Assignee: **Conoco Inc., Ponca City, Okla.**

[21] Appl. No.: **586,616**

[22] Filed: **Dec. 29, 1983**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 363,329, Mar. 29, 1982, abandoned.

[51] Int. Cl.⁴ **B01D 17/04**

[52] U.S. Cl. **252/348; 210/708;**

210/748; 252/331; 252/346

[58] Field of Search **252/331, 346, 348; 210/708, 748**

References Cited

U.S. PATENT DOCUMENTS

2,446,557 8/1948 Schutz et al. 252/346

OTHER PUBLICATIONS

Berkman et al.: "Emulsions and Foams", Reinhold Publ. Corp., New York, 1941, pp. 285-291.

Copson: "Microwave Heating", The Avi Publ. Co., Inc., Westport, Conn., 1962, pp. 371-373.

Primary Examiner—Richard D. Lovering
 Attorney, Agent, or Firm—Stephen A. Littlefield

ABSTRACT

Oil and water emulsions can be more rapidly separated when exposed to electromagnetic radiation in the range of from 1 to 300 millimeters, commonly called microwaves. The microwave treatment can be in conjunction with other separating and heating devices such as skimmers, gun barrel treaters, heater treaters, and the like.

12 Claims, 2 Drawing Figures

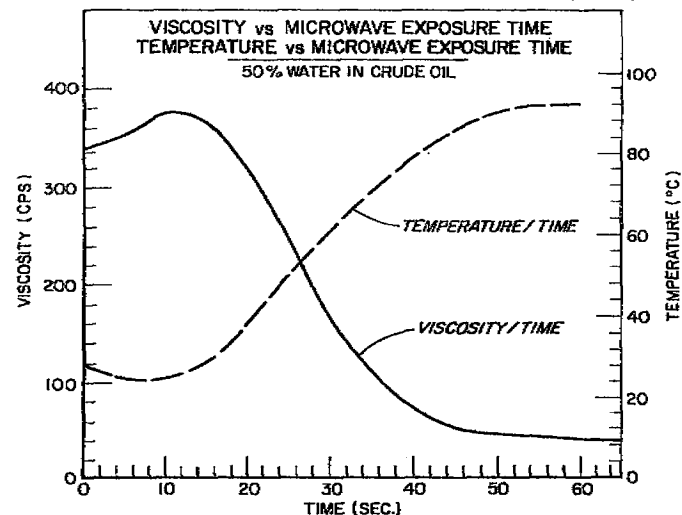
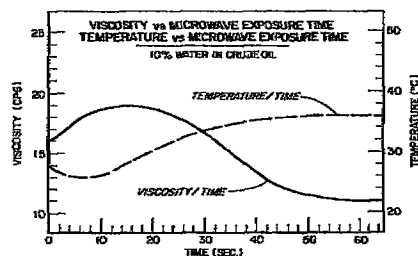


FIG. 2

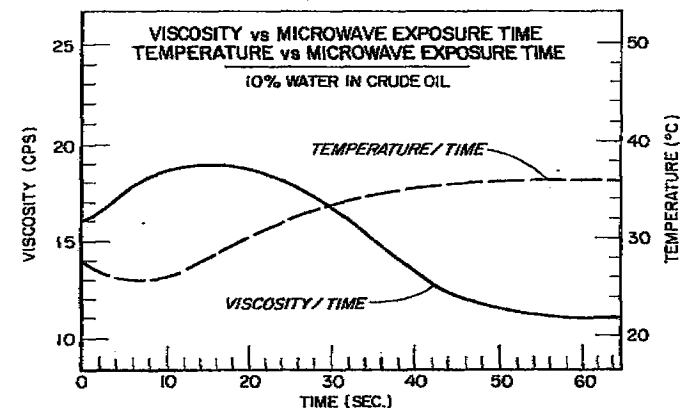


FIG. 1

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USE OF MICROWAVE RADIATION IN SEPARATING EMULSIONS AND DISPERSIONS OF HYDROCARBONS AND WATER

This application is a continuation-in-part of application Ser. No. 363,359, filed Mar. 29, 1982, and now abandoned.

The present invention relates to a method for enhancing the separation of oil and water dispersions and emulsions. More particularly, the present invention is concerned with enhancing separation of oil and water emulsions and dispersions by treating the same with microwave radiation, whether alone or in conjunction with more conventional separating devices.

In the petroleum industry, most of the crude oil produced is co-mingled with water and gas. It is therefore necessary to provide a means of sufficiently and economically separating the oil/water and gas for separate discharge. Usually the separated water is returned to a subterranean formation containing oil and the separated oil is conducted to a pipeline for ultimate transportation to a refinery and end use. Normally the separated gas is vented if in small quantities or if in commercial quantities collected for distribution and sale.

Primary production of oil from subterranean oil bearing reservoirs is normally obtained by exploiting the natural drive energy of the reservoir in the form of water drive, gas cap drive, solution gas drive, and combinations thereof. Oil remaining in the reservoir after primary energy sources have been depleted can be partially recovered by secondary recovery methods. One of the most common secondary recovery methods is waterflooding. Using this method flooding water is injected into the reservoir through one or more injection wells traversing the oil-bearing reservoir. The water displaces the oil in the reservoir and moves it through the reservoir toward one or more production wells from which oil is produced.

With the rising value of petroleum products it becomes increasingly important that separator equipment utilized by the petroleum industry extract the maximum possible recovered petroleum products from water and oil emulsions and dispersions. To this end improved separating vessels have been made from time to time over the years. Initially, the separators were merely open vessels providing a quiet zone with the intention that the water settle out and be withdrawn from the bottom of the vessel and that the petroleum float on the water be withdrawn from the top of the vessel. While this system is satisfactory to a degree, it nevertheless results in some oil remaining in the form of an emulsion with the withdrawn water and in like manner water being entrained with the oil withdrawn from the top of the vessel. Further, such gravitational settling processes are slow and require vessels of such volume that to allow separation by gravitation alone becomes exceedingly expensive and the reduced rate of flow results in general overall inefficiency.

Representative but non-exhaustive examples of various types of apparatus previously used in the art are gun barrel treaters, heater treaters, and the like. An apparatus specifically designed for use in separating oil and water can be found in, for example, U.S. Pat. No. 4,257,895. The use of ultrasonics is known for breaking hydrocarbon water emulsions as described in U.S. Pat. Nos. 2,257,997; 3,200,567; and 3,594,514. Other references disclose the application of microwave energy in

the recovery of oil from oil wells and oil shale such as U.S. Pat. Nos. 3,104,711; 3,133,592; 3,170,519 and 4,186,718. Microwaves have also been used in settling of solids and sewage sludge by using microwave energy such as described in U.S. Pat. No. 3,523,076.

However, none of these microwave references deal with the separation of oil/water emulsions and dispersions nor the necessity for increasing or enhancing the rate of separation therefrom. It would therefore be of great benefit to provide a method for enhancing the separation of such oil and water emulsions and dispersions.

It has now been discovered in accordance with the present invention that hydrocarbon and water emulsions and dispersions can be separated and the separation can be enhanced by the application of microwave radiation in the range of from 1 millimeter to 30 centimeters for a time sufficient to separate the dispersion or emulsion to the extent desired. Normally the microwave radiation will be used only for a short period of time, and the emulsion or dispersion will be heated to separation temperature by conventional means.

Microwave radiation as used in this specification and claims is defined in the Van Nostrand Scientific Encyclopedia, 1958, as extending from 300,000 MHz to 1,000 MHz or 1 millimeter (mm) to 30 centimeters (cm) in wavelength. Microwave frequencies between 2000 and 3000 MHz are preferred.

In general the microwave treatment of the oil/water emulsions or dispersions is carried out for an effective length of time. However, the emulsion or dispersion is normally treated at a power level of from about 1 watt to about 500 watts per gallon of emulsion or dispersion. This treatment is not sufficient to raise the temperature of the emulsion to levels normally used for separation, but will greatly enhance the resultant separation once heating is completed by conventional means.

The microwave radiation can be used in any desired wattage, but normally the higher the wattage used to produce the microwave radiation, the more quickly the dispersion or emulsion can be separated. The power used will range from a level of from about 300 to about 50,000 watts. Normally, microwave projectors in the wattage range of from about 800 to about 1000 watts will be used. For continuous treatment, a power level of from about 1 watt to about 500 watts per gallon of emulsion or dispersion will be used.

The microwave radiation of the present invention can be clearly distinguished from the ionizing radiation of the prior art. Ionizing radiation can be broken down into particulate and non-particulate radiation. Particulate radiation is generated from electronic accelerators such as residence transformers, linear transformers, insulated core transformers, and the like. Non-particulate ionizing radiation are sources which emit radiation in the range of about 10⁻³ angstroms to about 2000 angstroms. Suitable sources of this radiation are vacuum ultraviolet lamps such as xenon or krypton arcs and nuclear reactors. These radiations are completely distinguishable from the microwave radiations of the instant invention.

The temperature of the initial dispersion or emulsion will affect the amount of kilowatt power required to treat the dispersion or emulsion. Although the following is in part theoretical in nature and I do not wish to be bound thereby, it appears that microwave treating is a combination of two mechanisms. The first mechanism

is heating as in a conventional system. In this such a mechanism the microwave has the advantage of efficiency over conventional gas fired units. The second mechanism is connected with the excitation of bound water molecules which then disrupt surfactant molecules present in the interfacial film. Microwave treatment disrupts the emulsion and allows for more rapid separation of the oil and water. The temperature dependence of the power used in the process is mainly involved in the heating end, since water content will directly affect the extent to which a given microwave voltage applied will raise the temperature of the dispersion. Thus the colder the initial fluid and the higher the water content, the more power required.

The instant invention is applicable to both oil external and water external systems. In the area of temperature dependence, the difference between these systems is only in the amount of water to be heated. As oil absorbs roughly 100 times less microwave radiation than does water, the higher the incidence of water in the dispersion or emulsion, the more power required. Likewise, the higher the incidence of water, the more dramatic is the improvement in separation in oil-external systems. The instant invention is effective in oil external emulsions or dispersions containing more than 50% oil by weight based on the total weight of the emulsion or dispersion. Likewise, the system is effective in water external emulsions or dispersions containing from about 1% to about 50% oil by weight based on the total weight of the emulsion or dispersion.

The present invention can be used in combination with conventional treatment vessels such as heat treaters, which are tanks modified to add heat and provide residence time in the system. Microwaves would either be used directly in the tank to generate heat and interfacial disruption, or located in a section of the flow line just ahead of the tank. Likewise, the instant invention can be used in washbanks or gun barrel treaters, either in the tank or in the pipeline leading into the tank.

In practice, separation of emulsions and dispersions is carried out at temperatures of from about 45° C. to about 115° C. (to flash free water) but temperatures from 50° C. to 65° C. are more common and are preferred. The use of microwaves to enhance separation as described in the present invention raises the temperature of the dispersion or emulsion as previously described, but the best test is treatment of such materials to a temperature below that used for separation, then further increasing the temperature to separation levels. Whether used to completely heat the emulsion or dispersion, or to enhance separation without supplying all heat by microwave radiation, use of microwaves greatly facilitates separation of hydrocarbon-water emulsions and dispersions.

In general, there is a dramatic reduction in viscosity of emulsion subjected to microwave radiation. This reduction increases as time of exposure increases. Emulsions are much more easily broken as viscosity decreases. The microwave effect appears much greater than for externally supplied heat only.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphic representation of viscosity vs. microwave exposure time showing the effects of microwave in 10% water in crude oil composition. FIG. 2 is the same information presented for a 50% water in crude oil composition. The specific procedure

used in generating the data used to form the figures is set forth in Example 3.

The invention is more concretely described with reference to the examples below, wherein all parts and percentages are by weight unless otherwise specified. The examples are provided to illustrate the present invention and not to limit it. Microwave testing was accomplished using an International standard commercial microwave oven.

EXAMPLE 1

An experiment was carried out to determine the effect of microwaves on breaking emulsions prepared using both non-ionic and cationic surfactants. Two water-in-oil emulsions were prepared with tap water and crude oil in a ratio of 5:1 and one weight percent surfactant. In the first case, TETRAONIC (trademark of and sold by BASF Corp.) nonionic surfactant was used, in the second case a quaternary amine cationic surfactant was used. The emulsions were mixed in a blender prior to testing.

One hundred milliliters of each emulsion was poured into each of three glass bottles. One bottle was placed in a 60° C. (140° F.) bath as a blank. The remaining bottles were submitted to two 20 and two 30-second exposures in the microwave, which raised the samples to a temperature of 46° C. and 58° C. respectively; then placed in the bath along with the control to raise and maintain their temperature. The amount of oil, emulsion, and water present in each bottle was recorded after one hour. The results for each emulsion are shown in Table 1.

TABLE 1

	2-20-Second		2-30-Second	
	Blank	Exposures	Blank	Exposures
Oil Emulsion	40%	60%	70%	15%
Free Water	—	5%	15%	—
Oil Emulsion	100%	90%	—	—
Free Water	—	7%	—	10%

It is evident that the microwave did not have the same quantitative results, but it did improve breakout in all cases. This example clearly shows that microwaves benefited breakout time with a mechanism distinct from heating alone.

EXAMPLE 2

Microwave use enhances the effect of chemicals used to break oil/water emulsions. This effect will be seen when comparing use of microwaves and chemicals to chemical use alone, using the same procedure as described in Example 1.

An emulsion containing about 40% oil by volume which is especially difficult to break ("high" emulsion) will release about 15% of its bound water after 30 minutes when treated with 1000 parts per million of emulsion breaking chemicals (decanolifer, Nalco 4612, trademark of Nalco Chemical Co.) after heating to 60° C. The same sample, if treated with 30 seconds of microwave radiation (while containing 1000 ppm decanolifer) then heated to 60° C. will release about 70% of the bound water in 30 minutes.

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EXAMPLE 3

Viscosity changes as a result of microwave exposure were tested. Two dispersions were prepared, one containing 30% by volume water in crude oil, and a second containing 10% by volume water in crude oil. Each sample was blended at high speed for 5 minutes to produce a fresh "light" emulsion. Portions of each sample were then subjected to a variety of temperatures and various lengths of microwave exposure time. Viscosity changes of the samples were determined using a Brookfield viscometer. FIGS. 1 and 2 graphically illustrate the changes in viscosity found. The changes in both viscosity and temperature is proportionally much larger for the sample containing a larger quantity of water.

While certain embodiments and details have been shown for the purposes of illustrating this invention, it will be apparent to those skilled in this art that various changes and modifications may be made herein without departing from the spirit or scope of the invention.

I claim:

1. A method for enhancing the separation of hydrocarbon and water from an emulsion or dispersion thereof comprising the steps of subjecting said emulsion or dispersion to microwave radiation in the range of one millimeter to 30 centimeters and heating the microwave irradiated emulsion or dispersion to a separating temperature using conventional heating means.
2. A method as described in claim 1 when used at a power level of from about 300 to about 50,000 watts.
3. A method as described in claim 2 when used in oil external emulsions and dispersions.
4. A method as described in claim 3 wherein the oil external emulsion or dispersion contains from about

50% to greater than 99% oil by weight based on the total weight of the emulsion or dispersion.

5. A method as described in claim 4 wherein the emulsion or dispersion is treated at a power level of from about 1 watt to about 500 watts per gallon of emulsion or dispersion.

6. A method as described in claim 2 when used in water external emulsions and dispersions.

7. A method as described in claim 6 wherein the water external emulsion or dispersion contains from about 1% to about 50% oil by weight based on the total weight of the emulsion or dispersion.

8. A method as described in claim 7 wherein the emulsion or dispersion is treated at a power level of about 1 watt to about 500 watts per gallon of emulsion or dispersion in the presence of chemical deaerifiers.

9. A method as described in claim 8 wherein chemical deaerifiers are present at concentrations up to one percent by weight based on the weight of the dispersion or emulsion.

10. A method as described in claim 9 where the deaerifier is selected from the group consisting of non-ionic surfactants and cationic surfactants.

11. The method as described in claim 1 wherein said step of heating to a separating temperature comprises heating to a temperature of from about 45° C. to about 115° C.

12. A method for enhancing the separation of hydrocarbon and water from dispersion or emulsion thereof in the presence of chemical deaerifiers comprising the steps of contacting the dispersion or emulsion and chemical deaerifiers with microwave energy before heating the emulsion or dispersion to a separating temperature using conventional heating means.



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United States Patent [19]

Gregoli et al.

[11] Patent Number: 5,110,443

[45] Date of Patent: May 5, 1992

[54] CONVERTING HEAVY HYDROCARBONS
INTO LIGHTER HYDROCARBONS USING
ULTRASONIC REACTOR[58] Field of Search 252/312, 314, 330, 348;
264/41; 44/51, 301; 204/157.42; 208/106, 125,
46; 137/13[75] Inventors: Armand A. Gregoli, Tulsa, Okla.;
Andrew M. Olah, Spencer, Ohio;
John A. Hamsbur, Owasso; Daniel P.
Rimmer, Broken Arrow, both of
Okla.[73] Assignee: Canadian Occidental Petroleum Ltd.,
Calgary, Canada

[21] Appl. No.: 340,169

[22] Filed: Apr. 18, 1989

Related U.S. Application Data

[63] Continuation of Ser. No. 311,133, Feb. 14, 1989, abandoned, which is a continuation-in-part of Ser. No. 218,840, Jul. 14, 1988, Pat. No. 5,000,872, which is a continuation-in-part of Ser. No. 114,204, Oct. 27, 1987, Pat. No. 4,978,365, which is a continuation-in-part of Ser. No. 934,683, Nov. 24, 1986, Pat. No. 4,725,287.

[51] Int. Cl.⁵ C10G 15/08[52] U.S. Cl. 208/46; 44/301;
137/13; 204/157.42; 252/312; 252/314;
252/330; 252/348

[36] References Cited

U.S. PATENT DOCUMENTS

2,119,350	5/1938	Fier et al.	208/125
3,497,005	2/1970	Pelopsky et al.	208/106 X
4,618,348	10/1986	Hayes et al.	44/51
4,646,771	3/1987	Prasad et al.	137/13
4,666,457	5/1987	Hayes et al.	44/51
4,725,287	2/1988	Gregoli et al.	44/51

OTHER PUBLICATIONS

Berkman et al.: *Emulsions and Foams*, Reinhold Publishing Corp., New York (1941), pp. 281, 282 and 285-293.Primary Examiner—Richard D. Lovering
Attorney, Agent, or Firm—John Wade Carpenter

[57] ABSTRACT

A process for converting heavy hydrocarbons into lighter hydrocarbons. The process comprises forming an oil-in-aqueous phase emulsion and feeding the formed emulsion into an ultrasonic reactor wherein heavy hydrocarbons are converted into lighter hydrocarbons.

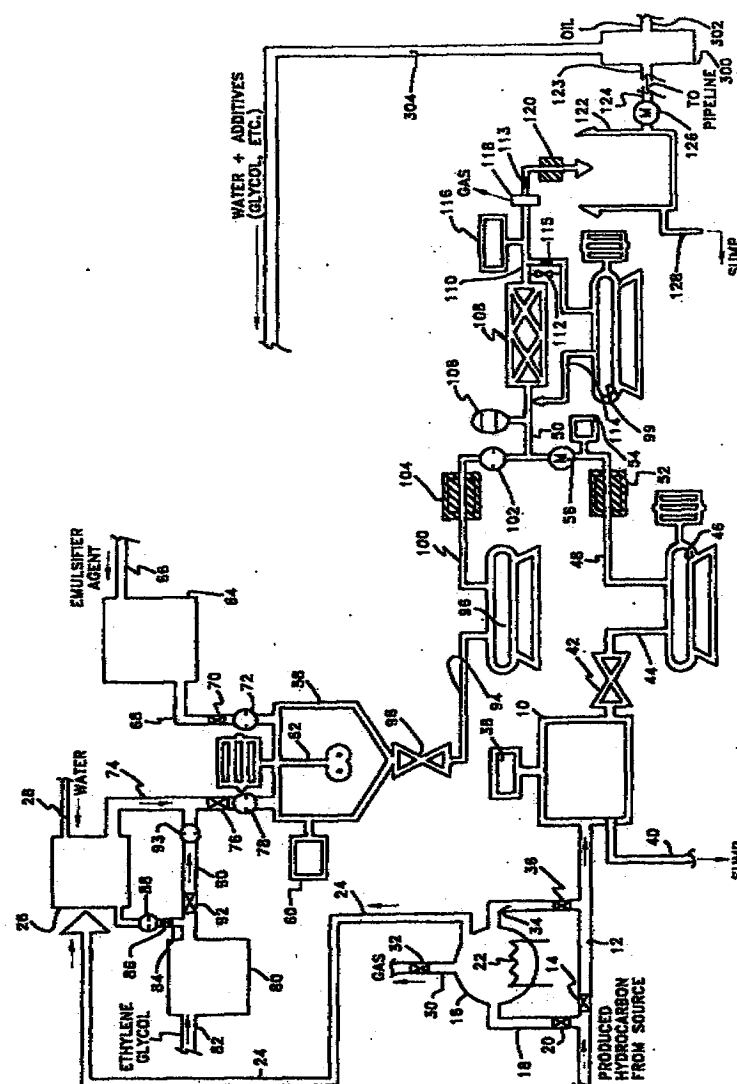
18 Claims, 10 Drawing Sheets

U.S. Patent

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ceptable period of time and with a commercially acceptable emulsion shear stability is the 5/15/5 mixture of DD 20/DD 70/DD 150 in combination with 75% by weight NP 20 agent. The weight average molecular weight for the DD mixture is 4171 (which is between 2434 and 4264) and the dispersity of 1.30 is between 1.0 and 5.0. Furthermore, the estimated quantity in percent by weight of DD compounds in the DD mixture having a molecular weight of between 2434 and 4264 is 55% by weight (which is greater than at least 50% by weight). The 15/5/5 mixture of DD 20/DD 70/DD 150 in combination with 75% by weight percent of the NP 20 agent did not produce within an acceptable period of time of less than about 20 secs. an acceptable oil-in-water emulsion having an emulsion shear stability greater than or equal to 40 mins. because the estimated quantity in percent by weight of DD compounds in the DD mixture having a molecular weight of 2434 to 4264 is 16.4% by weight (which is less than at least 50% by weight). If this estimated quantity in percent by weight is 30% by weight greater, an acceptable oil-in-water emulsion would be formed within an acceptable period of time. The 5/5/15 mixture of DD 20/DD 70/DD 150 in combination with 25% by weight of the NP 20 agent did not produce an acceptable oil-in-water emulsion because the estimated quantity in percent by weight of DD compounds in the 5/5/15 DD mixture having a molecular weight of 2434 to 4264 is 24% by weight (which is less than at least 50% by weight), and further because the weight average molecular weight of the mixture is 6281 (which is not between 2434 and 4264). If this estimated quantity in percent by weight is 50% by weight or greater and if the weight average molecular weight is between 2434 and 4264, an acceptable oil-in-water emulsion would be formed within an acceptable period of time.

EXAMPLE XXXXIII

Repeat Example XXXXII where the percent by weight of the NP 20 agent in the DD/NP 20 agent mixture is decreased to below about 60% by weight and the percent by weight of the respective DD compounds (i.e. DD 20, DD 70, and DD 100) in the DD/NP 20 agent mixture is varied and/or adjusted accordingly such that the weight average molecular weight of the DD mixture is 2434 and 4264, dispersity of the NP mixture is 1.0 to 5.0, and the estimated quantity in percent by weight of DD compounds in the DD mixture having a molecular weight between 2434 and 4264 is at least 50% by weight, and find that an acceptable oil-in-water emulsion is not formed and/or is not formed within an acceptable period of time.

EXAMPLE XXXXIV

Repeat Example XXXXIII where the percent by weight of the NP 20 agent in the DD/NP 20 agent mixture is increased above 65% by weight and find similar results.

EXAMPLE XXXXV

The emulsifying agent for this Example is the emulsifying agent of Example XXXXII comprising the 5/15/5 mixture of DD 20/DD 70/DD 150 in combination with 75% by weight NP 20 agent. The emulsifying agent is mixed with an aqueous phase (e.g. brine) at a temperature of about 200° F. to form an emulsifying composition with the emulsifying agent comprising from about 5% by weight to about 60% by weight of the emulsify-

ing composition. From about 2,000 to about 60,000 gallons of this emulsifying composition at a temperature of about 200° F. is injected into a heavy crude or tar sands formation via an injection or production well over a period of one to five days. The formation has a temperature of about 150° F. Subsequently, steam (75% to 100% quality) at 500° F. is injected into the formation for a period of 20 to 40 days at a rate of 600 to 1,500 barrels per day. The production well is thereafter shut in for one to ten days to allow the steam and emulsifying composition to soak in the formation. Subsequently, the production well is opened up and production of oil-in-aqueous phase emulsion is started with the assistance of a downhole pump at the bottle of the production well.

EXAMPLE XXXXVI

Repeat Example XXXXV but concurrently inject into the formation at a rate of about 1,000 barrels per day the emulsifying composition with the 500° F. steam such that the emulsifying composition enters into the formation at a temperature above P.T.T. (or about 210° F.) and the weight ratio of the 500° F. steam to the emulsifying composition is about 20:1. The weight ratio of the steam to emulsifying composition can vary from about 1:1 to about 50:1, and hot water having a temperature of 150° F. to 250° F. or hot water and steam can be substituted for the steam in the same weight ratio. After shutting in the production well for a soak period of 10 to 20 days wherein the emulsifying composition cools to below about P.T.T. (or about 210° F.) and oil-in-aqueous phase emulsion forms, the production well is opened up and the oil-in-aqueous phase emulsion is produced having a greater or enhanced stability than the oil-in-aqueous phase emulsion of Example XXXXV.

While the present invention has been described herein with reference to particular embodiments thereof and examples therefor, a latitude of modification, various changes and substitutions are intended in the foregoing disclosure and it will be appreciated that in some instances some features of the invention will be employed without a corresponding use of other features without departing from the scope of the invention as set forth. For example, while mixing of hydrocarbon crude with the emulsifying composition has been described as taking place above the surface of the earth, it is to be understood that mixing of hydrocarbon crude with the emulsifying composition below the surface of the earth, such as in a tubing of a producing well, is within the spirit and scope of this invention. Similarly, while the production of an oil-in-water emulsion has been described for purposes of transmission through a pipeline, it is to be understood that the spirit and scope of this invention include the production of an oil-in-water emulsion for any suitable purpose including, but not limited to, burning in a burner/boiler, and purposes of transmission through any pipe means. Thus, by way of example only, whenever "pipeline" is referred to in the specification and the claims, it is to be construed to be any pipe means, such as tubing of a producing well.

We claim:

1. A process for converting hydrocarbons and crudes into lighter hydrocarbon products comprising the steps of:

- (a) providing a hydrocarbon;
- (b) preparing an oil-in-aqueous phase emulsion containing the hydrocarbon; said preparing comprises:
 - (i) admixing water droplets with a catalyst;

- (ii) surrounding the water droplets containing the catalyst with droplets of the hydrocarbon;
- (iii) forming the oil-in-aqueous phase emulsion containing a multilamellar vesicle with the hydrocarbon droplets of step (ii) surrounded by the water droplets; and
- (c) feeding the oil-in-aqueous phase emulsion into an ultrasonic reactor for converting the hydrocarbon in the oil-in-aqueous phase emulsion into a lighter hydrocarbon product and to form residual oil-in-aqueous phase emulsion containing the lighter hydrocarbon product, the hydrocarbon, and gaseous reaction products.

2. The process of claim 1 wherein said catalyst is selected from the group consisting of zinc chloride, ferrous sulfate, ferric chloride, cobalt nitrate, stannous chloride, cadmium acetate, cupric chloride, manganese nitrate and silver nitrate.

3. The process of claim 1 wherein said catalyst is selected from the group consisting of sulfuric acid and hydrochloric acid.

4. The process of claim 1 wherein said catalyst is selected from the group consisting of ammonium molybdate and potassium molybdate ammonium vanadate.

5. The process of claim 1 wherein said catalyst is selected from the group consisting of cobalt naphthenate, nickel naphthenate, zinc naphthenate, tin naphthenate, iron naphthenate, copper naphthenate, cadmium naphthenate, and vanadium naphthenate.

6. The process of claim 1 additionally comprising passing the lighter hydrocarbon product, the residual oil-in-aqueous phase emulsion and the gaseous reaction products through a separator wherein the gaseous reaction products are removed.

7. The process of claim 6 additionally comprising adding a demulsifying chemical to said residual oil-in-aqueous phase emulsion after said gaseous reaction products have been removed.

8. The process of claim 7 additionally comprising heating the residual oil-in-aqueous phase emulsion and demulsifying chemical to break the residual oil-in-aqueous phase emulsion, separating aqueous phase from the broken residual oil-in-aqueous phase emulsion, and recycling the separated aqueous phase for preparing said oil-in aqueous phase emulsion in step (b).

9. The process of claim 7 additionally comprising heating the residual oil-in-aqueous phase emulsion and demulsifying chemical to break the residual oil-in-aqueous phase emulsion, separating the hydrocarbon from the broken residual oil-in-aqueous phase emulsion, and recycling the hydrocarbon for preparing said oil-in-aqueous phase emulsion in step (b).

10. A process for converting hydrocarbons and crudes into a lighter hydrocarbon products comprising the steps of:

- (a) providing a hydrocarbon;

- (b) preparing an oil-in-aqueous phase emulsion containing the hydrocarbon; said preparing comprises:
 - (i) admixing the hydrocarbon with a catalyst;
 - (ii) surrounding water droplets with droplets of the hydrocarbon containing the catalyst;
 - (iii) forming the oil-in-aqueous phase emulsion containing a multilamellar vesicle with the hydrocarbon droplets of step (ii) surrounded by the water droplets;

(c) feeding the oil-in-aqueous phase emulsion into an ultrasonic reactor for converting the hydrocarbon in the oil-in-aqueous phase emulsion into a lighter hydrocarbon product and to form residual oil-in-aqueous phase emulsion containing the lighter hydrocarbon product, the hydrocarbon, and gaseous reaction products.

11. The process of claim 10 wherein said catalyst is selected from the group consisting of cobalt stearates, nickel stearates, zinc stearates, tin stearates, iron stearates, copper stearates, cadmium stearates, and vanadium stearates.

12. The process of claim 10 wherein said catalyst is selected from the group consisting of cobalt sulfonates, nickel sulfonates, zinc sulfonates, tin sulfonates, iron sulfonates, copper sulfonates, cadmium sulfonates and vanadium sulfonates.

13. The process of claim 10 wherein said catalyst is selected from the group consisting of cobalt porphyrins, nickel porphyrins, zinc porphyrins, tin porphyrins, iron porphyrins, copper porphyrins, cadmium porphyrins and vanadium porphyrins.

14. The process of claim 10 wherein said catalyst is selected from the group consisting of metal sulfonates, dodecylbenzene metal sulfonates, and metal dinonyl naphthalene disulfonate.

15. The process of claim 10 additionally comprising passing the lighter hydrocarbon product, the residual oil-in-aqueous phase emulsion and the gaseous reaction products through a separator wherein the gaseous reaction products are removed.

16. The process of claim 15 additionally comprising adding a demulsifying chemical to said residual oil-in-aqueous phase emulsion after said gaseous reaction products have been removed.

17. The process of claim 16 additionally comprising heating the residual oil-in-aqueous phase emulsion and demulsifying chemical to break the residual oil-in-aqueous phase emulsion, separating aqueous phase from the broken residual oil-in-aqueous phase emulsion, and recycling the separated aqueous phase for preparing said oil-in-aqueous phase emulsion in step (b).

18. The process of claim 16 additionally comprising heating the residual oil-in-aqueous phase emulsion and demulsifying chemical to break the residual oil-in-aqueous phase emulsion, separating the hydrocarbon from the broken residual oil-in-aqueous phase emulsion, and recycling the hydrocarbon for preparing said oil-in-aqueous phase emulsion in step (b).

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