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**SUPERINTENDENCIA DE INDUSTRIA
DIVISION DE NUEVAS CREACIONES**

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Ref: 01035611-01035611
Fecha: 2001-07-15
Trámite: 1. ASO PATENTES 2. A REGISTRAR 3. AL COMITADO
Dependencia: EN LA DIVISION DE NUEVAS CREACIONES

REF: Expediente No.01 035.611 - Solicitud de Patente
a favor de INTEVEP, S.A.

Titulada: EMULSION DE AGUA EN HIDROCARBUROS UTIL COMO
COMBUSTIBLE DE BAJA EMULSION Y METODO DE FORMACION

RAMIRO CASTRO DUQUE, vecino de Bogotá, portador de la tarjeta profesional No. 1003, obrando como apoderado de la sociedad INTEVEP, S.A., según lo acredita el documento de poder protocolizado en esa División bajo el No. 14558, para dar cumplimiento al requerimiento notificado por fijación en lista el 31 de Mayo de 2001, y de acuerdo con los artículos 38 y 39 de la Decisión 486 de la comisión de la Comunidad Andina, me permito anexar al presente escrito los siguientes documentos:

1. Nos permitimos ACLARAR que el documento de poder fue protocolizado bajo el número 14558.
2. El lugar de constitución de la Sociedad solicitante es: Caracas, Venezuela.
3. Documento donde consta la cesión del derecho a la Patente otorgado por los inventores al solicitante, debidamente apostillado.
4. De acuerdo con lo solicitado nos permitimos informar que la modalidad de la presente solicitud es de PATENTE DE INVENCION.
5. Extracto para Publicación y Tarjeta de Archivo Temático.

848737/12

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(Convention de La Haye du 5 octobre 1961)

1. Country: United States of America

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6. the twenty-fourth of May, 2001

7. by Assistant Authentication Officer, United States Department of State

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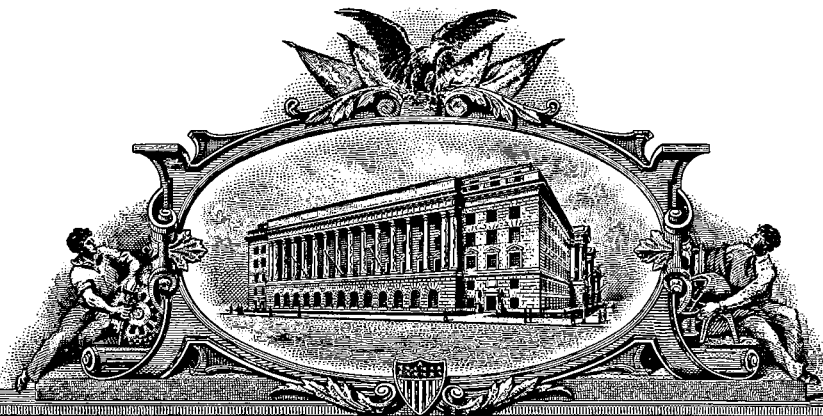


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OMB No. 0651-0011 (exp. 4/94)

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1 SHEET

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Hercilio Rivas Geoffrey McGrath
Xiomara Gutierrez Francisco Lopez-Linanes
Manuel A. Gonzales D. Roberto Galiasso
Migdalia Carrasquero
Additional name(s) of conveying party(ies) attached? ☐ Yes ☒ No

2. Name and address of receiving party(ies)

Name: INTEVEP, S.A.

Internal Address: Apartado 76343, Caracas
1010A, VENEZUELA

Street Address:

City: State: ZIP:

Additional name(s) & address(es) attached? ☐ Yes ☒ No

3. Nature of conveyance:

☒ Assignment ☐ Merger
☐ Security Agreement ☐ Change of Name
☐ Other

Execution Date: 4/16/00; 4/14/00; 4/13/00

4. Application number(s) or patent number(s):

If this document is being filed together with a new application, the execution date of the application is: 4/16/00; 4/14/00
4/13/00

A. Patent Application No.(s)

B. Patent No.(s)

Additional numbers attached? ☐ Yes ☒ No

5. Name and address of party to whom correspondence concerning document should be mailed:

Name: Gregory P. LaPointe

Internal Address: Suite 1201

Street Address: 900 Chapel Street

City: New Haven State: CT ZIP: 06510

6. Total number of applications and patents involved: ☐

7. Total fee (37 CFR 3.41).....\$ 40

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8. Deposit account number:

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Gregory P. LaPointe

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PATENT

REEL: 010782 FRAME: 0238

Assignment

In consideration of One Dollar (\$1.00), and other good and valuable consideration, the receipt of which is hereby acknowledged, we, the undersigned, Hercilio Rivas; Xiomara Gutierrez, Manuel A. Gonzalez D., citizens and residents of VENEZUELA; Geoffrey McGrath a citizen of Great Britain, resident of VENEZUELA; Migdalia Carrasquero, Francisco Lopez-Linares and Roberto Galiasso, all citizens and residents of VENEZUELA

Hereby sell, assign and transfer to INTEVEP, S.A.

a corporation of VENEZUELA

having a place of business at Apartado 76343, Caracas 1010A, VENEZUELA its successors, assigns and legal representatives, the entire right, title and interest for the United States and all foreign countries, in and to any and all improvements which are disclosed in the application for United States Letters Patent, which has been executed by the undersigned concurrently herewith

and is entitled WATER IN HYDROCARBON EMULSION USEFUL AS LOW EMISSION FUEL AND METHOD FOR FORMING SAME (Attorney's Docket No. 99-395)

, and in and to said application and all divisional, continuing, substitute, renewal, reissue, and all other applications for Letters Patent which have been or shall be filed in the United States and all foreign countries on any of said improvements; and in and to all original and reissued patents which have been or shall be issued in the United States and all foreign countries on said improvements;

Agree that said Assignee may apply for and receive Letters Patent for said improvements in its own name; and that, when requested, without charge to but at the expense of said Assignee, its successors, assigns and legal representatives, to carry out in good faith the intent and purpose of this assignment, the undersigned will execute all divisional, continuing, substitute, renewal, reissue, and all other patent applications on any and all said improvements; execute all rightful oaths, assignments, powers of attorney and other papers; communicate to said Assignee, its successors, assigns, and representatives, all facts known to the undersigned relating to said improvements and the history thereof; and generally do everything possible which said Assignee, its successors, assigns or representatives shall consider desirable for aiding in securing and maintaining proper patent protection for said improvements and for vesting title to said improvements and all applications for patents and all patents on said improvements, in said Assignee, its successors, assigns and legal representatives; and

Covenant with said Assignee, its successors, assigns and legal representatives that no assignment, grant, mortgage, license or other agreement affecting the rights and property herein conveyed has been made to others by the undersigned, and that full right to convey the same as herein expressed is possessed by the undersigned.

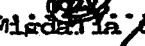
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Date 04/13/2000
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Hercilio Rivas (L.S.)

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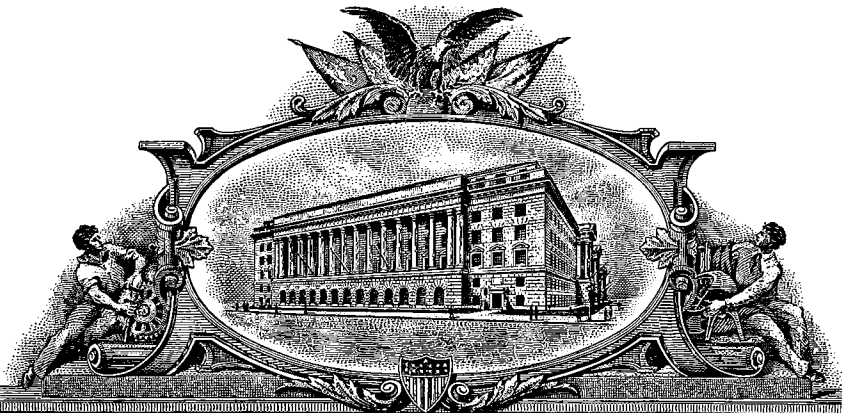
Roberto Galiasso

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PATENT
REEL: 010782 FRAME: 0239

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APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE UNDER 35 USC 111.**

APPLICATION NUMBER: 09/565,556

FILING DATE: May 05, 2000



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Case Docket No. 99-395

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Washington, D.C. 20231JCS15 U.S. PRO
09/56556
05/05/00

Sir:

Transmitted herewith for filing is the patent application of:

INVENTOR: HERCILIO RIVAS ET AL.

FOR: WATER IN HYDROCARBON EMULSION USEFUL AS LOW EMISSION FUEL AND
METHOD FOR FORMING SAME

Enclosed are:

- (~~XXX~~) Two sheets of drawing(s).
- (~~XXX~~) An Assignment of the invention to INTEVEP, S.A.
- () A certified copy of _____ Application
No. _____, Filed _____.
- () Verified statement(s) to establish small entity status
under 37 CFR 1.9 and 37 CFR 1.27.
- (~~XXX~~) INFORMATION DISCLOSURE STATEMENT, LISTING OF PRIOR ART ON
FORM PTO 1449 AND COPIES.

The filing fee has been calculated as shown below:

	No. Filed	No. Extra	SMALL ENTITY		OTHER THAN A SMALL ENTITY	
			Rate	Fee	Rate	Fee
For Basic Fee				\$ 345		\$ 690
Total Claims	33	- 20 = 13	x 9	\$	x 18	\$ 234
Indep Claims	2	- 3 = 0	x 39	\$	x 78	\$
Multiple Dependent Claim () Presented			+135	\$	+270	\$
			TOTAL	\$	TOTAL	\$ 924

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Date: May 5, 2000

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on MAY 5, 2000

Janice I. Staton

Name and Reg. No. of Attorney

Signature

Date of Signature

GREGORY B. LAPOINTE

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APPLICATION FOR LETTERS PATENT

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT Hercilio Rivas, Xiomara Gutierrez, Manuel A. Gonzalez D., Geoffrey McGrath, Migdalia Carrasquero, Francisco Lopez-Linares and Roberto Galiasso all citizens and residents of VENEZUELA have invented certain new and useful improvements in WATER IN HYDROCARBON EMULSION USEFUL AS LOW EMISSION FUEL AND METHOD FOR FORMING SAME of which the following is a specification

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May 5, 2000

Date of Deposit

Janice I. Staton

Name and Title of Inventor

Date of Signature

potentially hazy water saturated alcohol-gasoline mixture into a clear stable gasoline composition having an improved octane rating. The system so produced has a water content of no more than 1% by volume, and relatively large volumes of non-ionic surfactant are used to produce this system.

Similarly, U.S. Patent Nos. 4,770,670 and 4,744,796 to Hazbun et al. also disclose the formation of stable microemulsions which contain large amounts of surfactant as compared to the water content.

Other efforts in this area include U.S. Patent No. 5,104,418, WO 99/35215, U.S. Patent No. Re.35,237, U.S. Patent No. 5,743,922, WO 97/34969, U.S. Patent No. 5,873,916 and WO 99/13031.

In spite of the disclosures in the a foregoing patents, the need remains in the industry for a water-in-hydrocarbon emulsion which is suitable as a combustible fuel and which contains a desirable amount of water without the need for relatively large amounts of surfactant and/or other stabilizing agents.

It is therefore the primary object of the present invention to provide water-in-hydrocarbon emulsions which are useful as combustible fuels and which are both stable and formed using relatively small amounts of surfactant.

It is a further object or the present invention to provide a method for forming such water-in-hydrocarbon emulsions

utilizing a synergetic combination of mixing energy and surfactant package blend.

It is a still further object of the present invention to provide emulsions and methods for forming such emulsions wherein additional combustion properties are incorporated into the fuel through the surfactant package.

Other objects and advantages of the present invention will be readily apparent from a consideration of the following.

SUMMARY OF THE INVENTION

In accordance with the present invention, the foregoing objects and advantages have been readily attained.

In accordance with the invention, a water-in-hydrocarbon emulsion is provided, which emulsion comprises a water phase, a hydrocarbon phase and a surfactant, wherein said water phase is present in an amount greater than or equal to about 5% vol. with respect to volume of said emulsion, and said water phase and said surfactant are present at a ratio by volume of said water phase to said surfactant of at least about 1.

Stable macroemulsions and microemulsions are provided, each having advantageous features and characteristics.

In further accordance with the invention, a method is provided for forming a water-in-hydrocarbon emulsion which method comprises the steps of providing a water phase; providing

a hydrocarbon phase; providing a surfactant; mixing said water phase, said hydrocarbon phase and said surfactant in amounts sufficient to provide a water content of at least about 5% vol. with respect to said emulsion, and a ratio by volume of said water phase to said surfactant of at least about 1, wherein said mixing is carried out at a mixing intensity sufficient to form a stable emulsion of said water phase in said hydrocarbon phase.

BRIEF DESCRIPTION OF THE DRAWINGS

005050-050500
A detailed description of preferred embodiments of the present invention follows, with reference to the attached drawings, wherein:

Figure 1 is a schematic representation illustrating the mechanism of the mixing process of the present invention;

Figure 2 is a comparative illustration of cylinder pressure versus crank angle of a base fuel as compared to a water-in-hydrocarbon fuel prepared in accordance with the present invention;

Figure 3 is a comparative illustration of NO_x exhaust gas emission rates at steady state conditions for a base fuel and an emulsion in accordance with the present invention;

Figure 4 is a comparative illustration of cumulative carbon exhaust gas emission during engine transient operation utilizing

a base fuel and an emulsion in accordance with the present invention;

Figure 5 is a comparative illustration of exhaust gas peak opacity during free acceleration for a base fuel and an emulsion in accordance with the present invention; and

Figure 6 is an illustration of interfacial tension versus concentration of monoethanolamine and the expected characteristics of the interface depending upon same.

DETAILED DESCRIPTION

0050500

The invention relates to water-in-hydrocarbon emulsions and a method for forming same whereby the emulsion is stable and can advantageously be used as a combustible fuel, for example for compression ignition engines and the like. The emulsion has beneficial characteristics as a fuel including reduced emissions. The emulsions in accordance with the present invention include stable macroemulsions and microemulsions, each of which include a dispersed water phase and a continuous hydrocarbon phase as well as an advantageous surfactant package which, as will be discussed below, is preferably selected in combination with particular emulsion formation mixing intensities, so as to provide the desired stable emulsion.

Suitable hydrocarbons for use in making the emulsions of the present invention include petroleum hydrocarbons and natural

gas derived products, examples of which include Diesel fuel and other low gravity hydrocarbons such as Fischer-Tropsch synthetic Diesel and paraffins C₁₀ to C₂₀.

Emulsions including this hydrocarbon in accordance with the present invention have reduced NO_x emissions and C emissions, and improved opacity as compared to the hydrocarbon alone.

Further, improvement in air-fuel mixing conditions and of evaporative spray in the combustion chamber of Diesel engines can be accomplished utilizing the emulsion as compared to the base fuel, which can result in improvements in the fuel fraction efficiency and a better energy balance utilization in combination with the lower exhaust gas and particulate emissions. One example of a suitable hydrocarbon is a Diesel fuel characterized as follows:

Table 1

Sulfur content	(% wt/wt)	<0.5
Density @ 15°C	(kg/m ³)	<860
Viscosity @ 40°C	(mm ² /s)	<4.5
T95	(°C)	<370
Flash point	(°C)	>52

The water phase for use in forming emulsions in accordance with the present invention can suitably be from any acceptable water source, and is preferably a water which is available in

sufficient quantities, preferably in close proximity to the location where emulsions are to be formed, and preferably at an inexpensive cost. For example, a suitable water phase could be water such as 310 ppm brine. Of course, any other water from a suitable source and having various acceptable characteristics for use as a component of a combustible fuel would be acceptable.

The surfactant package forms an important portion of the present invention, particularly when combined with particular emulsion forming steps as will be further described below. The surfactant or surfactant package of the present invention is preferably a package including both a lipophilic surfactant component and a hydrophilic surfactant component. This combination of components advantageously serves to increase the amount of molecules which are present at the water-hydrocarbon interface, and to minimize the interfacial tension therein, thereby allowing substantially reduced amounts of surfactants to be utilized while nevertheless providing a stable emulsion. This is particularly advantageous from a cost standpoint as compared to conventional known emulsions and processes.

Suitable surfactants, as set forth above, include both lipophilic surfactant components and hydrophilic surfactant components. Suitable lipophilic surfactant components include neat oleic acid, sorbitan ester monooleate, sorbitan ester

trioleate, ethoxylated oleic acid and mixtures thereof. These lipophilic surfactant components typically have a hydrophile-lipophile balance, or HLB, of between about 1 and about 8. The hydrophile-lipophile balance or HLB of a surfactant is the relative simultaneous attraction that the surfactant demonstrates for water and oil. Substances having a high HLB, above about 12, are highly hydrophilic while substances having a low HLB, below about 8, are highly lipophilic. Surfactants having an HLB between about 8 and about 12 are considered intermediate.

Suitable hydrophilic surfactant components include oleic acid which has been neutralized, preferably 100% neutralized, with monoethanolamine, polyethoxylated fatty amine and mixtures thereof. These hydrophilic surfactant components typically have an HLB of between about 10 and about 18.

Neutralized oleic acid may be formed as hydrophilic surfactant component by mixing, either separately or during emulsion formation, neat oleic acid and monoethanolamine (MEA) whereby oleate ions are formed as further discussed below.

Additional components such as cosolvents for microemulsions, and other additives, may also be present.

As will be discussed more thoroughly below in connection with the process for forming the emulsion, surfactant components which are both lipophilic and hydrophilic are preferably

selected and mixed for use in forming the emulsion, and this advantageously results in the formation of an interface in the emulsion between the water phase and the hydrocarbon phase which includes a mixture of both surfactant components.

Microemulsions according to the invention are advantageously provided with a ratio by volume of water to surfactant which is greater than about 1. Macroemulsions according to the invention are advantageously formed with very small amounts of surfactant, preferably less than or equal to about 4% vol., and having a ratio by volume of water to surfactant of greater than about 2.5.

005050-050500
The emulsions of the present invention preferably include water by volume with respect to the emulsion in an amount of at least about 5%, preferably between about 5% vol. and about 15% vol. with respect to total volume of the emulsions. As will be illustrated in the data to follow, the particular surfactant package and the mixing intensity or energy dissipation rate of the present invention both appear critical in providing acceptably stable emulsions.

It should also be noted that the emulsion of the present invention as compared to a base fuel from which the emulsion was prepared compares favorably in connection with engine cylinder pressure versus crank angle, NO_x exhaust gas emission, carbon exhaust gas emission, exhaust gas peak opacity and the like.

As set forth above, it is also within the scope of the present invention to modify the surfactant package so as to include additional functional groups which can be selected so as to provide desirable properties in the resulting emulsion fuel.

For example, a nitro-olefin derivate of oleic acid can be obtained, for example by using nitrogen monoxide to modify the oleic acid. Such a nitro-olefin derivate of oleic acid can be utilized during emulsion formation and remains active in the final emulsion as a cetane number improver for providing the emulsion with a higher cetane number as compared to a microemulsion formed with a normal oleic acid as a component of the surfactant package. Of course, other functional groups, particularly other nitrogen functional groups, could advantageously be incorporated into the surfactant package for various other desirable results. Other functional groups that can advantageously be incorporated into the surfactant package include ketones, hydroxy and epoxy groups, and the like.

Emulsions in accordance with the present invention may suitably be formed as described below.

Suitable supplies of both water phase and hydrocarbon phase are obtained.

Once it is determined what type of emulsion is desired, that is, a microemulsion or a macroemulsion, a suitable surfactant package is selected.

Referring to Figure 1, the steps of the method of the present invention are illustrated in terms of the type of droplet size formed and status of the surfactant. The process preferably starts the formation of a coarse dispersion which is refined and homogenized by turbulence-length scales of decreasing size (through mixing mechanisms associated with turbulent diffusion). The final stage of mixing involves microscale engulfment and stretching where the ultra low surface tension results in the formation of a microemulsion. Where no ultra-low interfacial tension is achieved, the fineness of the dispersion, for a given surfactant package, depends upon the intensity of the turbulence.

In order to prepare a microemulsion, the surfactant package is preferably selected including a hydrophilic component and a lipophilic component which are balanced so as to provide a surfactant package HLB of between about .6 and about 10. This surfactant package will be acceptable when utilized in conjunction with the additional process steps of the present invention for providing a stable microemulsion.

In order to form a suitable microemulsion, the three components, that is, the water phase, hydrocarbon phase and surfactant package are preferably combined in the desired volumes and subjected to a mixing intensity (W/kg) which is selected in accordance with the present invention in order to

provide the desired type of emulsion. In accordance with the invention, to form a microemulsion, it is desirable to utilize a surfactant package having an HLB between about 6 and about 10 and a mixing intensity of between about 1 W/kg and about 10,000 W/kg. On an in-line production scale, the mixing intensity is more preferably between about 100 and about 1000 W/kg. If production rates are not critical, average mixing intensities between about 1 W/kg and about 100 W/kg also provide a stable microemulsion. Mixing according to the invention advantageously results in a desirable stable microemulsion having an average droplet size of between about 100Å and about 700Å. Emulsions formed according to the invention are advantageously stable in that the emulsion will retain an average droplet diameter, when stored under normal ambient conditions, for at least about 1 year and typically for an indefinite period of time.

The mixing intensity referred to herein is presented as average mixing intensity, averaged over the mixing profile of a vessel. Depending upon the mixing intensity and mixing time used, different orders of mixing intensity can be encountered within the mixing vessel. For example, mixing can be accomplished in accordance with the present invention utilizing a Rushton impulsor coupled to a Heidolph motor for providing the desired mechanical energy dissipation rate or mixing intensity. In a typical vessel mixed with this equipment, while the vessel

As set forth above, the surfactant package can advantageously be modified so as to include performance improving functional groups such as nitro-groups and the like which advantageously serve to improve the cetane number of the final emulsion product.

Macroemulsions are formed in accordance with the present invention as follows. As with microemulsion preparation supplies of suitable water and hydrocarbon phases are obtained.

A surfactant package is then preferably selected having an HLB of between about 3 and about 10. As with the microemulsions, this HLB is obtained by blending lipophilic and hydrophilic surfactant components as described above, in proportions sufficient to provide the desired HLB. The water, hydrocarbon and surfactant package components are then mixed at a mixing intensity selected so as to provide the desired macroemulsion, preferably having an average droplet size of between about 0.5 and about 2.0 microns. It is preferred that the macroemulsion be mixed at a mixing intensity of greater than or equal to about 10,000 W/kg, and this mixing intensity corresponds to an energy dissipation rate during turbulent flow as with the microemulsion formation process. The acceptable mixing intensity can be imparted to the mixture of ingredients using known equipment which would be readily available to the person of ordinary skill in the art.

course be noted that mixing intensities much larger than average can be encountered in the mixing vessel, for example near the mixing apparatus.

Microemulsions were prepared utilizing 5% volume of water (310 ppm brine), a hydrocarbon phase of Diesel fuel as described above in Table 1 and surfactant packages including one or more components of lipophilic neat oleic acid (HLB = 1.3), lipophilic sorbitan ester monooleate (HLB = 4.3) and lipophilic ethoxylated oleic acid (5 EO, HLB = 7.7), and hydrophilic oleic acid 100% neutralized with monoethanolamine.

The first samples of emulsion prepared under this example were prepared using a surfactant package including a lipophilic surfactant component of oleic acid having an HLB of 1.3 and a hydrophilic oleic acid 100% neutralized with monoethanolamine (oleate ions, HLB = 18). These components were provided in a 1:1 ratio by volume and utilized to form emulsions as set forth in Table 2 below:

TABLE 2

Sample No.	Surfactant	Vol.% Diesel	Vol.% Surfactant	Vol.% Mono ethanol amine	Vol.% Deionized Water (310 ppm Brine)	Vol.% n-Hexanol	HLB	Mixing Intensity W/kg	Obs.
1	Neat Oleic Acid/Oleic Acid 100% neutralized with monoethanol amine	84.6	8 (4/4)	0.86	5	1.5	9.5	Manual agitation	Micro emulsion
2	Neat Oleic Acid/Oleic Acid 100% neutralized with monoethanol amine	89.1	4 (2/2)	0.43	5	1.5	9.5	1	Micro emulsion
3	Neat Oleic Acid/Oleic Acid 100% neutralized with monoethanol amine	89.1	4 (2/2)	0.43	5	1.5	9.5	Manual agitation	Unstable Macro emulsion

Sample 1 was prepared using 8% volume of surfactant package and a mixing intensity generated through manual agitation of about 0.1 W/kg or less for approximately 2-5 minutes (spontaneous formation). Sample 2 was prepared utilizing 4% volume of surfactant package and moderate turbulence utilizing a Rushton impulsor coupled to a Heidolph motor for providing an average mechanical energy dissipation rate of 1 W/kg for a period of approximately 5 minutes. Sample 3 was prepared also utilizing 4% volume of the surfactant package, but with manual agitation of less than 0.1 W/kg as with Sample 1.

As shown in Table 2, Sample 1 resulted in a microemulsion, but required 8% volume of surfactant. Sample 3 utilizing 4%

volume of the surfactant package and manual agitation resulted in an unstable macroemulsion.

Sample 2, prepared in accordance with the present invention, provided a stable microemulsion utilizing only 4% volume of surfactant package which is, of course, advantageous as compared to the 8% volume required for Sample 1.

Samples 4-5 were then prepared utilizing the same surfactant package and 10% volume of water. Sample 4 was prepared utilizing 14% volume of surfactant package and manual agitation. Sample 5 was prepared using 7% volume of surfactant package and a vessel averaged mixing intensity of 1 W/kg. Sample 6 was prepared utilizing 7% volume of surfactant package and manual agitation.

Table 3 sets forth the results obtained for these samples.

TABLE 3

Sample No.	Surfactant	Vol.% Diesel	Vol.% Surfactant	Vol.% Mono ethanol amine	Vol.% Deionized Water (310 ppm Brine)	Vol.% n-Hexanol	HLB	Mixing Intensity W/Kg	Obs.
4	Neat Oleic Acid/Oleic Acid 100% neutralized with monoethanol amine	73.6	14 (7.6/6.4)	1.40	10	1.0	8.9	Manual agitation	Micro emulsion
5	Neat Oleic Acid/Oleic Acid 100% neutralized with monoethanol amine	81.3	7 (3.8/3.2)	0.70	10	1.0	8.9	1	Micro emulsion
6	Neat Oleic Acid/Oleic Acid 100% neutralized with monoethanol amine	81.3	4 (3.8/3.2)	0.70	10	1.0	8.9	Manual agitation	Unstable Macro emulsion

TABLE 4

Sample No.	Surfactant	Vol.% Diesel	Vol.% Surfactant	Vol.% Mono ethanol amine	Vol.% Deionized Water (310 ppm Brine)	Vol.% n-Hexanol	HLB	Mixing Intensity W/Kg	Obs.
7	Neat Oleic Acid/Oleic Acid 100% neutralized with monoethanol amine	61.3	20 (10/10)	2.15	15	1.5	9.5	Manual agitation	Micro emulsion
8	Neat Oleic Acid/Oleic Acid 100% neutralized with mono ethanol amine	68	14 (7/7)	1.51	15	1.5	9.5	1	Micro emulsion
9	Neat Oleic Acid/Oleic Acid 100% neutralized with monoethanol amine	68	14 (7/7)	1.51	15	1.5	9.5	Manual agitation	Unstable Macro emulsion

As shown, Sample 7 resulted in a stable microemulsion, but required more surfactant than water was present. Sample 9 utilized less surfactant package, but resulted in an unstable macroemulsion.

Sample 8, prepared in accordance with the present invention, provided a stable microemulsion having a ratio of water to surfactant of greater than 1.

Samples 10-12 were prepared utilizing a surfactant package including lipophilic sorbitan ester monooleate having an HLB of 4.3 and neat oleic having HLB equal to 1.3, and hydrophilic oleic acid which has been 100% neutralized with monoethanolamine (oleate ions, HLB = 18). Samples 10 and 12 were prepared

acid/base reaction in the interface Diesel/water to give rise to the oleate ions. The oleic acid as well as the oleate ions are adsorbed in the interface Diesel/water due there infinity to the water as the oil. At intermediate concentrations of MEA (0.04-0.3% volume), the oleic acid is appreciably ionized so as to provide oleate ions, and the interface Diesel/water will be covered by both oleate ions and oleic acid. In this zone, synergistic interfacial tension is illustrated, since the interfacial tension is lower than that obtained from either of the surfactants individually.

It should be appreciated that a water-in-hydrocarbon emulsion has been provided which exhibits advantageous characteristics as compared to conventional fuels, and that methods for advantageously forming such emulsions have also been provided.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

129
128WHAT IS CLAIMED:

1. A water-in-hydrocarbon emulsion comprising a water phase, a hydrocarbon phase and a surfactant, wherein said water phase is present in an amount greater than or equal to about 5% vol. with respect to volume of said emulsion, and said water phase and said surfactant are present at a ratio by volume of said water phase to said surfactant of at least about 1.

2. An emulsion according to claim 1, wherein said emulsion is a microemulsion having an average droplet size of between about 100Å and about 700Å.

3. An emulsion according to claim 1, wherein said hydrocarbon phase is a low gravity hydrocarbon.

4. An emulsion according to claim 1, wherein said hydrocarbon phase is selected from the group consisting of Diesel fuel, natural gas derived products and mixtures thereof.

5. An emulsion according to claim 1, wherein said hydrocarbon phase is Diesel fuel.

6. An emulsion according to claim 1, wherein said surfactant comprises a mixture of a lipophilic surfactant

005050-050500

15
130

11. An emulsion according to claim 1, wherein said surfactant further includes a functional group for improving performance of said emulsion as a combustible fuel.

12. An emulsion according to claim 11, wherein said functional group is a nitrogen oxide group.

13. An emulsion according to claim 1, wherein said emulsion is a macroemulsion having an average droplet size of between about 0.5 and about 2.0 microns.

14. An emulsion according to claim 13, wherein said surfactant comprises an emulsion stabilizing portion which consists essentially of a lipophilic surfactant component having an HLB of between about 1 and about 8 and a hydrophilic surfactant component having an HLB of between about 10 and about 18 whereby solvents are not needed for forming a stable macroemulsion.

15. An emulsion according to claim 13, wherein said macroemulsion is substantially free of cosolvents.

32
132

mixing intensity sufficient to form a stable emulsion of said water emulsion phase in said hydrocarbon phase.

20. A method according to claim 19, wherein said mixing is carried out at a mixing intensity of between about 1 W/kg and about 10,000 W/kg and said surfactant is selected having an HLB of between about 6 and about 10 so as to provide a microemulsion having an average droplet size of between about 100Å and about 700Å.

21. A method according to claim 20, wherein said mixing intensity is between about 1 W/kg and about 100 W/kg.

22. A method according to claim 20, wherein said mixing step further includes mixing said water phase, said hydrocarbon phase and said surfactant with a cosolvent in amount by volume of less than or equal to about 2% with respect to said emulsion.

23. A method according to claim 22, wherein said cosolvent is selected from the group consisting of methanol, ethanol, isopropanol, n-propanol, n-butanol, ter-butanol, n-pentanol, n-hexanol and mixtures thereof.

005050-050500

54
133

24. A method according to claim 19, wherein said mixing is carried out at a mixing intensity of greater than or equal to about 10,000 W/kg and said surfactant is selected having an HLB of between about 3 and about 10 so as to provide a macroemulsion having an average droplet size of between about 0.5 microns and about 2.0 microns.

25. A method according to claim 24, wherein said surfactant comprises an emulsion stabilizing portion which consists essentially of a lipophilic surfactant portion having an HLB of between about 1 and about 8 and a hydrophilic surfactant portion having an HLB of between about 10 and about 18 whereby cosolvents are not needed for forming a stable macroemulsion.

26. A method according to claim 24, wherein said macroemulsion is substantially free of cosolvents.

27. A method according to claim 19, wherein said surfactant comprises a mixture of a lipophilic surfactant component having a hydrophile-lipophile balance of between about 1 and about 8, and a hydrophilic surfactant component having a hydrophile-lipophile balance of between about 10 and about 18.

005050-050500

Practitioner's Docket No. 99-395

PATENT

COMBINED DECLARATION AND POWER OF ATTORNEY
(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL,
CONTINUATION, OR C-I-P)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type:

(check one applicable item below)

- ☒ original.
☐ design.
☐ supplemental.

NOTE: If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.

- ☐ national stage of PCT.

NOTE: If one of the following 3 items apply, then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR C-I-P.

NOTE: See 37 C.F.R. § 1.63(d) (continued prosecution application) for use of a prior nonprovisional application declaration in the continuation or divisional application being filed on behalf of the same or fewer of the inventors named in the prior application.

- ☐ divisional.
☐ continuation.

NOTE: Where an application discloses and claims subject matter not disclosed in the prior application, or a continuation or divisional application names an inventor not named in the prior application, a continuation-in-part application must be filed under 37 C.F.R. § 1.53(b) (application filing requirements — nonprovisional application).

- ☐ continuation-in-part (C-I-P).

INVENTORSHIP IDENTIFICATION

WARNING: If the inventors are each not the inventors of all the claims, an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

WATER IN HYDROCARBON EMULSION USEFUL AS LOW EMISSION FUEL
AND METHOD FOR FORMING SAME

(Declaration and Power of Attorney [1-1]—page 1 of 7)

157
136

0955555-050500

139
138

SUPPLEMENTAL DECLARATION (37 C.F.R. § 1.67(b))

(complete the following where a supplemental declaration is being submitted)

- ☐ I hereby declare that the subject matter of the
- ☐ attached amendment
 - ☐ amendment filed on _____

was part of my/our invention and was invented before the filing date of the original application, above-identified, for such invention.

ACKNOWLEDGEMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, § 1.56,

(also check the following items, if desired)

- ☒ and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent, and
- ☒ In compliance with this duty, there is attached an information disclosure statement, in accordance with 37 C.F.R. § 1.98.

PRIORITY CLAIM (35 U.S.C. §§ 119(a)-(d))

NOTE: "The claim to priority need be in no special form and may be made by the attorney or agent if the foreign application is referred to in the oath or declaration as required by § 1.63. The claim for priority and the certified copy of the foreign application specified in 35 U.S.C. 119(b) must be filed in the case of an interference (§ 1.630), when necessary to overcome the date of a reference relied upon by the examiner, when specifically required by the examiner, and in all other situations, before the patent is granted. If the claim for priority or the certified copy of the foreign application is filed after the date the issue fee is paid, it must be accompanied by a petition requesting entry and by the fee set forth in § 1.17(f). If the certified copy is not in the English language, a translation need not be filed except in the case of interference; or when necessary to overcome the date of a reference relied upon by the examiner; or when specifically required by the examiner, in which event an English language translation must be filed together with a statement that the translation of the certified copy is accurate." 37 C.F.R. § 1.55(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §§ 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

- (d) ☒ no such applications have been filed.
- (e) ☐ such applications have been filed as follows.

NOTE: Where item (c) is entered above and the International Application which designated the U.S. itself claimed priority check item (e), enter the details below and make the priority claim.

(Declaration and Power of Attorney [1-1]—page 3 of 7)

0050500-050500

140
139

**PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION
AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119(a)-(d)**

COUNTRY (OR INDICATE IF PCT)	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 37 USC 119
			☐ YES NO ☐
			☐ YES NO ☐
			☐ YES NO ☐
			☐ YES NO ☐
			☐ YES NO ☐

**CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)
(34 U.S.C. § 119(e))**

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

PROVISIONAL APPLICATION NUMBER

FILING DATE

_____/_____
_____/_____
_____/_____

**CLAIM FOR BENEFIT OF EARLIER US/PCT APPLICATION(S)
UNDER 35 U.S.C. § 120**

- ☐ The claim for the benefit of any such applications are set forth in the attached ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CONTINUATION-IN-PART (C-I-P) APPLICATION.

(Declaration and Power of Attorney [1-1]—page 4 of 7)

00500-9550-3560

141
140

**ALL FOREIGN APPLICATION(S), IF ANY, FILED MORE THAN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION**

NOTE: If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete **ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR C-I-P APPLICATION** for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. § 120.

POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

(list name and registration number)

Robert H. Bachman (19,374); Gregory P. LaPointe (28,385); Barry L. Kelmachter (29,999) and George A. Coury (34,309)

(check the following item, if applicable)

- ☐ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.
- ☐ Attached, as part of this declaration and power of attorney, is the authorization of the above-named practitioner(s) to accept and follow instructions from my representative(s).

SEND CORRESPONDENCE TO

DIRECT TELEPHONE CALLS TO:
(Name and telephone number)

☒ Address

BACHMAN & LAPOINTE, P.C.
900 Chapel Street
Suite 1201
New Haven, CT 06510-2802

Gregory P. LaPointe
(203) 777-6628, Ext. 111

☐ Customer Number _____

142
141

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

NOTE: Carefully indicate the family (or last) name, as it should appear on the filing receipt and all other documents.

NOTE: Each inventor must be identified by full name, including the family name, and at least one given name without abbreviation together with any other given name or initial, and by his/her residence, post office address and country of citizenship. 37 CFR § 1.63(a)(3).

NOTE: Inventors may execute separate declarations/oaths provided each declaration/oath sets forth all the inventors. Section 1.63(a)(3) requires that a declaration/oath, inter alia, identify each inventor and prohibits the execution of separate declarations/oaths which each sets forth only the name of the executing inventor. 62 Fed. Reg. 53,131, 53,142, October 10, 1997.

Full name of sole or first inventor

Hercilio Rivas
(GIVEN NAME) (MIDDLE INITIAL OR NAME) (FAMILY (OR LAST NAME))

Inventor's signature [Signature]

Date 04/16/2000 Country of Citizenship Venezuela

Residence Av. Leopoldo Amador, Guatopo 6-93, Sta Fe Norte, Caracas Venezuela

Post Office Address 76343, Caracas 1070, Venezuela

Full name of second joint inventor, if any

Xiomara Gutiérrez
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Inventor's signature [Signature]

Date 04/14/2000 Country of Citizenship Venezuela

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Full name of third joint inventor, if any

Manuel A. González
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Inventor's signature [Signature]

Date 09/14/2000 Country of Citizenship VENEZUELA

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Post Office Address 76343, CARACAS 1070, VENEZUELA

(Declaration and Power of Attorney [1-1]—page 6 of 7)

005050-95500

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142

(check proper box(es) for any of the following added page(s)
that form a part of this declaration)

☒ Signature for fourth and subsequent joint inventors. Number of pages added
1

. . .

☐ Signature by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. Number of pages added _____

. . .

☐ Signature for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR 1.47. Number of pages added _____

. . .

☐ Added page for signature by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 CFR 1.47)

. . .

☐ Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application.

☐ Number of pages added _____

. . .

☐ Authorization of practitioner(s) to accept and follow instructions from representative.

. . .

(if no further pages form a part of this Declaration,
then end this Declaration with this page and check the following item)

This declaration ends with this page.

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ADDED PAGE TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR SIGNATURE BY FOURTH AND SUBSEQUENT INVENTORS

Full name of fourth joint inventor, if any

Geoffrey

(GIVEN NAME)

(MIDDLE INITIAL OR NAME)

McGrath

FAMILY (OR LAST NAME)

Inventor's signature

Date 4/25/2000

Country of Citizenship GREAT BRITAIN

Residence MANSION ESTORIL, 4th AVENUE, LOS PALOS

GRANDES, CARACAS VENEZUELA

APDO 76343 MIRANDA VENEZUELA

Full name of fifth joint inventor, if any

Migdalena

(GIVEN NAME)

(MIDDLE INITIAL OR NAME)

Carrasquero

FAMILY (OR LAST NAME)

Inventor's signature

Date 04/14/2000

Country of Citizenship Venezuela

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Post Office Address 76343 Miranda - Venezuela

Full name of sixth joint inventor, if any

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(GIVEN NAME)

(MIDDLE INITIAL OR NAME)

López - Lirares

FAMILY (OR LAST NAME)

Inventor's signature

Date 04/13/2000

Country of Citizenship Venezuela

Residence C.R.C. LA HORITA TORRE B APTD 14143B San Antonio de los

ALTO - MIRANDA VENEZUELA

APDO POSTAL 76343

Full name of seventh inventor, if any

Roberto

(GIVEN NAME)

(MIDDLE INITIAL OR NAME)

Gallasso

FAMILY (OR LAST NAME)

Inventor's signature

Date 04/25/2000

Country of Citizenship VENEZUELA

Residence Av Principal Los Gatos Casa 235 SAN ANTONIO DE

LOS ACTOS LOS SALAS ESTADO MIRANDA

VENEZUELA

APDO 76343 MIRANDA VENEZUELA

Added Page to Combined Declaration and Power of Attorney for Signature by Fourth and Subsequent Inventors (1-2)

005050-9550-3560

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143

125
144

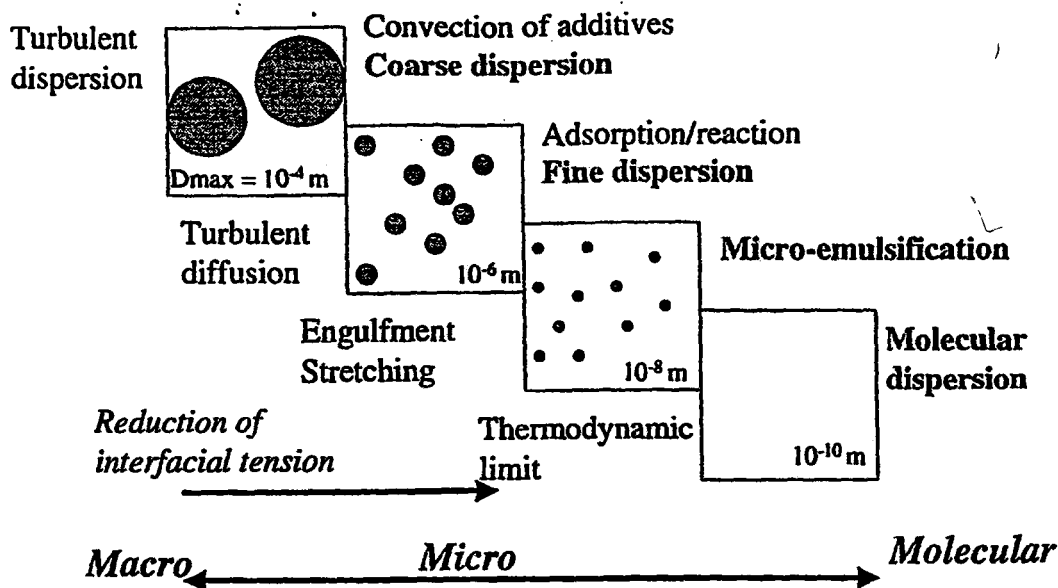


FIGURE 1

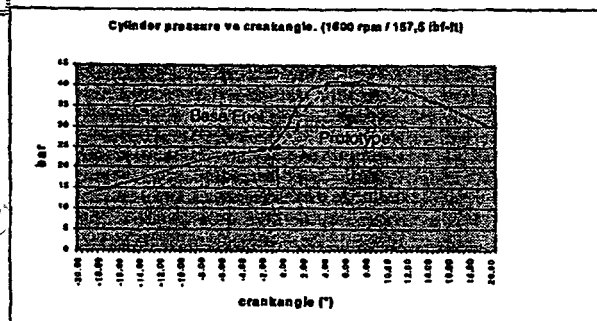


FIGURE 2

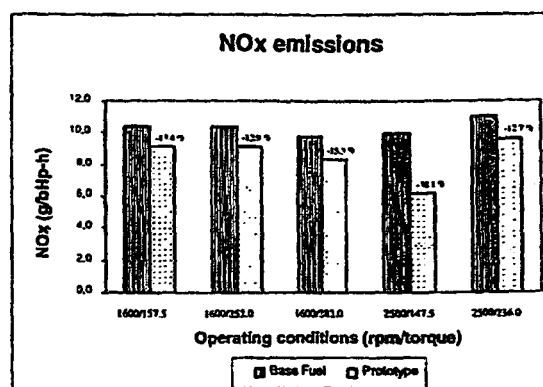


FIGURE 3

146
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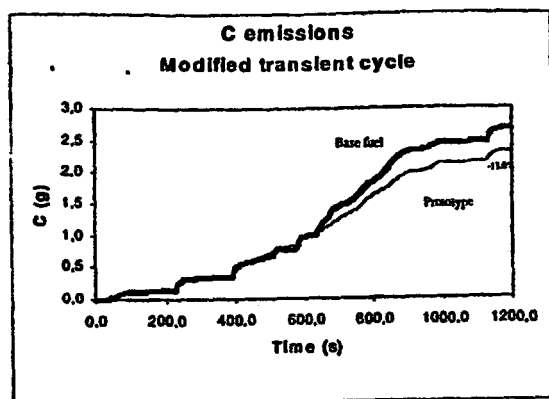


FIGURE 4

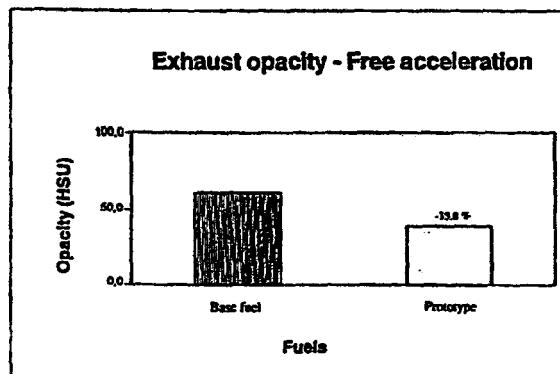


FIGURE 5

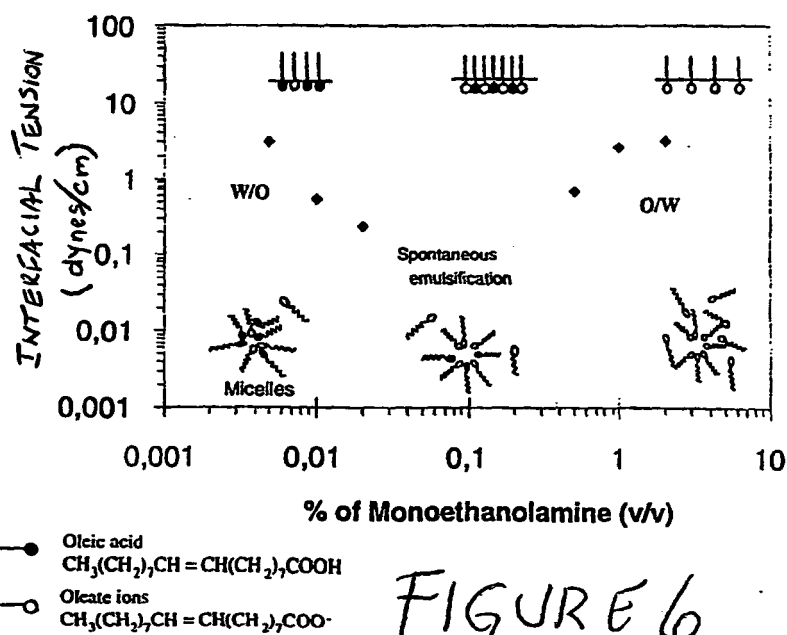


FIGURE 6