

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 01-013611- -00007-0000

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Tra 2 PATENTES Eve: 1 REGDEPOSITO
Act. 444 RESPUESTAREQUE Folios: 18

As. 84.875

Señora

JEFE DE DIVISIÓN DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

E.

S.

D.

REF: Expediente No. 01 035 611 – solicitud de patente de invención
a favor de INTEVEP S.A.

Respuesta a oficio No. 13629 del 18 de octubre de 2007

JUAN PABLO CADENA SARMIENTO, portador de la tarjeta profesional No. 57.492 del C.S.J., obrando como apoderado de la sociedad INTEVEP S.A., según lo acredita el documento de poder adjunto, manifiesto que ASUMO el conocimiento de las diligencias que se adelantan en el presente, y para dar cumplimiento al Artículo 45 de la Decisión 486 del Acuerdo de Cartagena me permito dar respuesta a las observaciones de carácter técnico y jurídico, relacionadas con la patentabilidad, para la concesión de la patente de según el concepto técnico No. 1894 notificado por fijación en lista de fecha 18 de octubre de 2007.

Atendiendo a las observaciones del señor examinador respecto a la claridad de la solicitud nos permitimos presentar un nuevo capítulo reivindicatorio de 1 – 18 reivindicaciones el cual reemplaza completamente las reivindicaciones anteriormente presentadas.

El capítulo reivindicatorio anexo elimina el uso de palabras ambiguas , especificando aun más el objeto y la materia de la solicitud, subsanando así las objeciones presentadas por el señor examinador.

El señor examinador objeta las reivindicaciones de método porque, en opinión del mismo, se pretende proteger un método que no se está definiendo. Según el señor examinador el uso de la palabra "proporcionar" es errado porque, según la real academia de la lengua esta palabra significa "Disponer y ordenar algo con la debida correspondencia de sus partes"; y, por lo tanto, "proporcionar un ingrediente" no especifica como se dispone y ordena dicho ingrediente. Al respecto cabe anotar que la Real Academia de la Lengua Española también define "Proporcionar" como: "Poner en aptitud o disposición las cosas, a fin de conseguir lo que se desea". Por consiguiente la etapa o paso de "proporcionar" un ingrediente es perfectamente válida, puesto que se están disponiendo una serie de cosas, en este caso ingredientes, para lograr un fin deseado, en este caso la composición.

Prosigue el señor examinador objetando la etapa de mezclado por no definir de manera precisa el paso y las cantidades de cada ingrediente. El respecto cabe anotar que el nuevo capítulo reivindicatorio anexo subsana esta objeción, definiendo de manera completa la etapa de mezclado del método.

Prosigue el señor examinador objetando la forma como el solicitante define la composición resultante. De acuerdo con el señor examinador, establecer que la composición tiene un contenido de agua de 5% en volumen y una proporción de 1 a 1 en volumen con el surfactante es inadmisibile, por tratarse de un resultado a obtener. Al respecto cabe anotar que en un campo tan amplio como el de las emulsiones existen muy pocas formas de diferenciar unas de otras, particularmente cuando el campo de aplicación es la industria de la explotación petrolífera. Las emulsiones que se utilizan en los pozos de petróleo tienen una finalidad muy similar y deben cumplir condiciones muy especiales, dado el ambiente en el que operan. Teniendo en cuenta lo anterior, es claro que la única forma de diferenciar dichas emulsiones es por sus composiciones, las cuales se definen como las proporciones de cada uno de los ingredientes respecto a un ingrediente específico, o respecto al total de la emulsión. Si una emulsión contiene mayor o menor cantidad de un ingrediente determinado, y esto proporciona un resultado nuevo e inesperado, entonces dicha emulsión es claramente

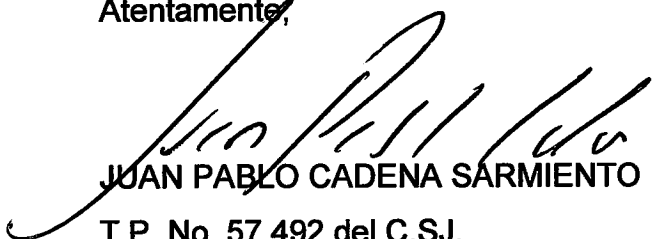
novedosa e inventiva por sobre el arte previo, y la única forma de definir y diferenciar dicha emulsión es por su contenido del ingrediente en cuestión. Dado lo anterior, se le solicita respetuosamente al señor examinador que acepte la definición de las emulsiones de la presente solicitud por la proporción de sus ingredientes.

Por último, el señor examinador cita una serie de documentos del arte previo que afectan la novedad y la altura inventiva de la presente solicitud, argumentando que el número de anterioridades obedece a la extrema amplitud de la materia divulgada. El nuevo capítulo reivindicatorio especifica aun más la materia objeto de la presente solicitud, y es claramente novedoso e inventivo por sobre los documentos del arte previo citados en la observación.

En vista de lo anterior, respetuosamente solicitamos el retiro de las objeciones a la presente solicitud, en base al nuevo capítulo reivindicatorio anexo, el cual no afecta en ningún sentido el alcance de la invención y, en opinión del solicitante, cumple a cabalidad con los requisitos de claridad, novedad, nivel inventivo y aplicabilidad industria exigidos por la Decisión 486.

De la Señora Jefe,

Atentamente,


JUAN PABLO CADENA SARMIENTO

T.P. No. 57.492 del C.SJ.

C.C. 80.410.337 de Usaquén

Carrera 7 No. 71-21, Torre B, Of. 402

Bogotá, Enero 10 de 2007

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Anexos

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4/208REIVINDICACIONES

1. Una microemulsión de agua en hidrocarburos líquidos estable CARACTERIZADA porque comprende una fase acuosa, una fase de hidrocarburo líquida y un conjunto de surfactantes que tiene un HLB de entre 6 y 10 y que comprende un componente surfactante lipofílico que tiene un HLB de entre 1 y 8 y un componente surfactante hidrofílico que tiene un HLB de entre 10 y 18, en donde dicha fase acuosa y dicho conjunto de surfactantes se encuentran presentes en una relación en volumen de dicha fase acuosa a dicho conjunto de surfactantes de al menos 1, en donde dicha fase acuosa está presente en una cantidad entre 5% en volumen y 15% en volumen con respecto al volumen de dicha microemulsión, y en donde dicho componente hidrofílico y dicho componente lipofílico están presentes en una interfase entre dicha fase acuosa y dicha fase de hidrocarburo líquido, y en donde dicho componente lipofílico comprende un derivado nitro olefínico del ácido oleico.

2. La microemulsión de acuerdo con la reivindicación 1, CARACTERIZADA porque dicha microemulsión estable tiene un tamaño promedio de gota pequeña de entre 100 Å y 700 Å.

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3. La microemulsión de acuerdo con la reivindicación 1 o 2, CARACTERIZADA porque dicha microemulsión contiene cosolvente en una cantidad menor que o igual a 2% en volumen con respecto al volumen de dicha microemulsión.

4. La microemulsión de acuerdo con la reivindicación 3, CARACTERIZADA porque dicho cosolvente se selecciona del grupo que consiste en metanol, etanol, iso-propanol, n-butanol, ter-butanol, n-pentanol, n-hexanol y mezclas de los mismos.

5. La microemulsión de acuerdo con la reivindicación 1, CARACTERIZADA porque dicho componente lipofílico se selecciona del grupo que consiste en ácido oleico puro, éster de sorbitán monooleato, éster de sorbitán trioleato, ácido oleico etoxilado y mezclas de los mismos.

6. La microemulsión de acuerdo con la reivindicación 1, CARACTERIZADA porque dicho componente hidrofílico se selecciona del grupo que consiste en ácido oleico neutralizado con monoetanolamina, amina grasa polietoxilada y mezclas de los mismos.

7. La microemulsión de acuerdo con una de las reivindicaciones 1 a 6, CARACTERIZADA porque dicho conjunto

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de surfactantes además incluye un grupo funcional para mejorar el comportamiento de dicha microemulsión estable como un aceite combustible, siendo dicho grupo funcional seleccionado del grupo que consiste en grupos funcionales con nitrógeno, cetonas, grupos epoxi e hidroxil, y mezclas de los mismos.

8. La microemulsión de acuerdo con una de las reivindicaciones 1 a 7, CARACTERIZADA porque dicho grupo funcional es un grupo óxido de nitrógeno.

9. La microemulsión de acuerdo con una de las reivindicaciones 1 a 8, CARACTERIZADA porque dicha fase de hidrocarburo se selecciona del grupo que consiste en combustible Diesel, combustible Diesel sintético Fischer-Tropsch, parafinas y mezclas de los mismos.

10. Un método para preparar una microemulsión de agua en hidrocarburos líquidos estable de acuerdo con una de las reivindicaciones 1 a 9, CARACTERIZADO porque comprende los pasos de:

proporcionar una fase de hidrocarburo líquido;

proporcionar una fase acuosa;

proporcionar un conjunto de surfactantes que tiene un HLB de entre 6 y 10 y que comprende un componente

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surfactante lipofílico que tiene un HLB de entre 1 y 8 y un componente hidrofílico que tiene un HLB de entre 10 y 18;

mezclar dicha fase de hidrocarburo líquido, dicha fase acuosa, y dicho conjunto de surfactantes en una relación en volumen de dicha fase acuosa a dicho surfactante de al menos 1, con dicha fase acuosa en una cantidad de entre 5% en volumen y 15% en volumen con respecto al volumen de dicha microemulsión y a una intensidad de mezcla de entre 1 W/kg y 10.000 W/kg, a fin de proporcionar una microemulsión de hidrocarburo líquido en agua estable en donde dicho componente hidrofílico y dicho componente lipofílico están presentes en una interfase entre dicha fase acuosa y dicha fase de hidrocarburo líquido, y en donde dicho componente lipofílico comprende un derivado nitro olefínico del ácido oleico.

11. El método de acuerdo con la reivindicación 10, CARACTERIZADO porque dicha intensidad de mezcla se encuentra entre 1 W/kg y 100 W/kg.

12. El método de acuerdo con la reivindicación 10 u 11, CARACTERIZADO porque dicha microemulsión estable tiene un tamaño promedio de gota pequeña entre 100 Å y 700 Å.

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13. El método de acuerdo con la reivindicación 10 o 12, CARACTERIZADO porque dicho paso de mezcla incluye además mezclar dicha fase acuosa, dicha fase de hidrocarburo líquido y dicho conjunto de surfactantes con un cosolvente en una cantidad en volumen menor que o igual a 2% con respecto a dicha microemulsión.

14. El método de acuerdo con una de las reivindicaciones 10 a 13, CARACTERIZADO porque dicho cosolvente se selecciona del grupo que consiste en metanol, etanol, isopropanol, n-butanol, ter-butanol, n-pentanol, n-hexanol y mezclas de los mismos.

15. El método de acuerdo con la reivindicación 10, CARACTERIZADO porque dicho componente surfactante lipofílico se selecciona del grupo que consiste en ácido oleico puro, éster de sorbitán monooleato, éster de sorbitán trioleato, ácido oleico etoxilado y mezclas de los mismos.

16. El método de acuerdo con la reivindicación 10, CARACTERIZADO porque dicho componente surfactante hidrofílico se selecciona del grupo que consiste en ácido oleico neutralizado con monoetanolamina, amina grasa polietoxilada y mezclas de las mismas.

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República Bolivariana de Venezuela

MINISTERIO DEL INTERIOR Y JUSTICIA

OFICINA PRINCIPAL DE REGISTRO
PÚBLICO DEL ESTADO MIRANDA



LEGALIZACIÓN

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cualquier Juez, corporación, funcionario público o autoridad en acciones judiciales, administrativas y de policía; tales como: oposiciones al registro de marcas; acciones de caducidad, cancelación y nulidad; acciones reivindicatorias, acciones derivadas de la obtención o explotación. A este efecto, los faculto para elevar solicitudes, formular descripciones, enmiendas, protestas, declaraciones, oposiciones, cancelaciones, nulidades, apelaciones y reclamos; pagar impuestos, cuotas y gravámenes prescritos por la ley; renunciar o desistir a derechos concedidos o en curso de concesión; recibir toda clase de documentos y valores, dando el descargo respectivo y, en general, para dar ante dichas autoridades todos los pasos necesarios al efecto indicado y tomar todas las medidas que creyeren conducentes al resguardo de los intereses de mi poderdante, con todas las demás facultades legales necesarias. Este poder comprende la facultad de ratificar o confirmar en nombre de mi otorgante lo actuado; así como, la facultad de desistir, transigir, comprometer sobre derechos concedidos o en curso de concesión, previa autorización del otorgante. Asimismo, nombro, en representación de **INTEVEP, S.A.** a: **JUAN PABLO CADENA SARMIENTO** y/o **BEATRIZ JARAMILLO** y/o **CARLOS H. PALACIO EASTMAN** y/o **HÉCTOR GÓMEZ MEJÍA**, todos domiciliado(s) en la Carrera 7, N° 16-56, Piso 9, apoderados especiales en Colombia, con facultades para recibir notificaciones y las previamente establecidas en este documento. Finalmente, revoco la sustitución de poder otorgada por mi a los señores **RAMIRO CASTRO DUQUE** y/o **JUAN PABLO CADENA SARMIENTO** y/o **BEATRIZ JARAMILLO S.**, según consta de documento autenticado por

ante la Notaría Pública del Municipio Guaicaipuro del estado Miranda, el día 28 de marzo de 2003, bajo el N° 49, Tomo 32 de los libros de autenticaciones llevados por esta Notaría, legalizado por ante la Oficina Principal de Registro del estado Miranda, el día 28 de marzo de 2003, posteriormente, presentado por ante el Ministerio de Interior y Justicia, Dirección General de Registros y Notarías, el día 1 de abril de 2003 y luego apostillado de conformidad con el Convenio de La Haya del 5 de octubre de 1961, por ante el Ministerio de Relaciones Exteriores, Dirección General de Relaciones Consulares, el día 4 de abril de 2003, bajo el N° 026972. En Los Teques, a la fecha de su presentación y autenticación.

CONSULTORIA
INTEVEP

REPUBLICA BOLIVARIANA
DE VENEZUELA
ESTADO MIRANDA

Intevsep S.A.
NOMBRE DEL SOLICITANTE

BEATRIZ JARAMILLO
NOMBRE DEL SOLICITANTE

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NÚMERO DE IDENTIFICACIÓN

00097678
CONCEPTO

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BASE LEGAL

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DIEZ MIL BOLÍVARES

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Ramiro Castro Duque

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REPUBLICA BOLIVARIANA DE VENEZUELA
MINISTERIO DEL INTERIOR Y JUSTICIA

NOTARIA PUBLICA DEL MUNICIPIO GUAICAIPURO. ESTADO MIRANDA. Los

Catorce (14) de Mayo De DOS MIL CINCO
(2.005).- 194° y 146° El anterior documento redactado por el Abogado: CARLOS ENRIQUE

FLORES, Inscrito en el inpreabogado bajo el N° 32.550, Fue presentado para su Autenticación y Devolución según planilla N° 189632, de fecha: 10-03-2005. Presente (s) su (s) otorgante (s) dijo (eron) ser y llamarse: **BLANCA MATILDE NAVARRO LAGUNA** mayor (es) de edad, domiciliado (s) en: LOS TEQUES, de nacionalidad: VENEZOLANA de estado civil:

DIVORCIADA portador (es) de la (s) Cédula (s) de Identidad No. V-3.829.465 Leído y confrontado con sus fotocopias, firmado en estas y en el presente original, en presencia del Notario el(los) Otorgante(s) expuso(ieron) "SU CONTENIDO ES CIERTO Y

MIA(NUESTRAS) LA(S) FIRMA(S) QUE LO AUTORIZA(N)". El Notario en tal virtud, da

Fe Pública del presente documento y de las copias firmadas en originales que formaran el Tomo

Principal y el Tomo Duplicado en presencia de los testigos: LOURDES PERDOMO y

JUDITH BRICEÑO, titulares de las Cédulas de Identidad Nros: V-8.682.840 y V-

6.870.509 dejándolo inserto bajo el Nro. 81 Tomo: 30 de los libros de Autenticaciones llevados

por esta Notaría. El Notario que suscribe hace constar que ha dado cumplimiento al Artículo

78 del Decreto Ley de Registro y del Notariado e informó a las partes del contenido, naturaleza,

trascendencia y consecuencias legales de los actos o negocios otorgados en su presencia, los

cuales manifestaron su plena conformidad. FUE INUTILIZADOS TIMBRES FISCALES POR

BOLIVARES 30.000,00. Igualmente le fue presentado Registro Mercantil de **ENVEVE S.A.**

debidamente en el Registro Mercantil Primero de la Circunscripción Judicial del Distrito Federal

y Estado Miranda de fecha: 31 de mayo de 1979, bajo el

reformada su Acta Constitutiva Estatutos en diversas oportunidades, siendo la última forma

parcial la inscrita en el Registro Mercantil Segundo de la citada Circunscripción Judicial

en fecha 17 de agosto de 1999, bajo el No. 17, Tomo: 227-A Segundo y finalmente

refundido en un solo texto dicho documento Constitutivo Estatutos según consta de

documento inscrito ante la citada Oficina de Registro en fecha: 5 de junio de 2000 bajo el

No. 72, Tomo: 128-A Sgdo. Representada en este acto por su apoderada Especial



CIENTO NOVENTA Y SIETE (197) VTO.

ciudadana: BLANCA MATILDE NAVARRO LAGUNA según documento
autenticado por ante esta misma Notaria en fecha: 18-03-2003, anotado bajo el No. 92;
tomo: 27 La Notaria para este acto se traslado y constituyo en la sede de. INTEVEP
S.A., Estado Miranda, a las 10:30 AM. fue autorizada para este acto la
ciudadana: JUDITH BRICEÑO Titular de la cédula de identidad No. 6.870.509
funcionaria de esta Notaria. Conforme al Artículo 29 del Reglamento de Registro
Notaria Publica

EL NOTARIO PUBLICO

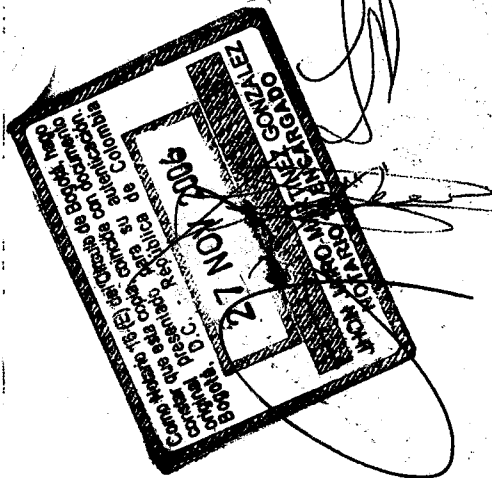


[Signature]
Dra. Judith del Carmen Escalona Aquino
NOTARIO INTERINO

EL (LOS) OTORGANTE (S)

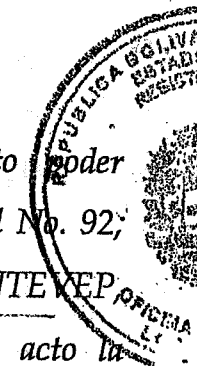
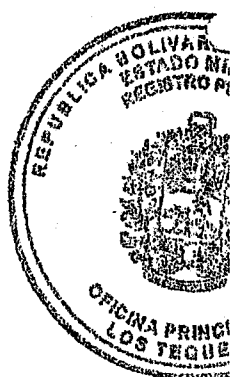
[Signature]
BLANCA MATILDE NAVARRO LAGUNA

LOS TESTIGOS



Otorgado por:

[Signature]



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ABOGADO
REVISADO

Nº 013777

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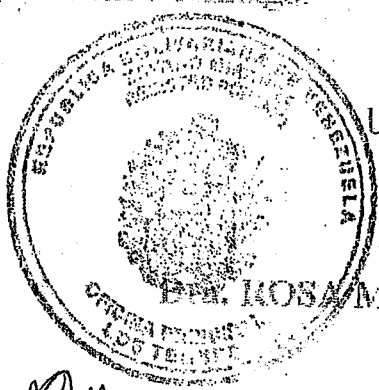
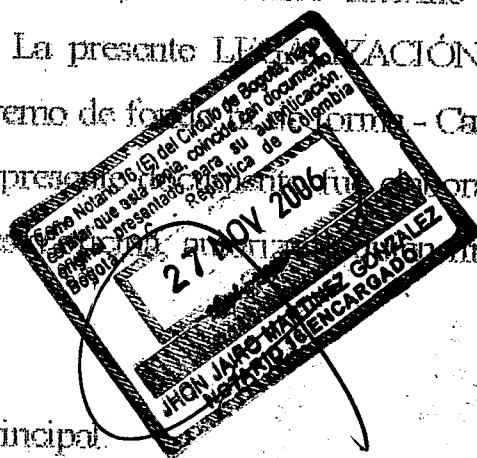
REPUBLICA BOLIVARIANA DE VENEZUELA
MINISTERIO DEL INTERIOR Y JUSTICIA

OFICINA PRINCIPAL DE REGISTRO PUBLICO DEL ESTADO MIRANDA

Los Teques, Diez y Seis (16) de Marzo del año 2005

AÑOS: 194º Y 146º

La Suscrita Registradora Principal del Estado Miranda, CERTIFICA que la firma que legaliza del anterior documento es autentica y la misma que utiliza en todos sus actos Públicos la ciudadana: Dra. MARÍA DEL CARMEN ESCALONA AQUINO. Quien para la fecha de la expedición del anterior documento a los Catorce (14) días del mes de Marzo del año 2005, era Notario Interino del Municipio Guacaipuro del Estado Miranda. La presente LEGITIMACIÓN se expide sin prejuzgar acerca de ningún otro extremo de forma. - Causó Derechos de Registro y Timbres Fiscales.- El presente documento fue elaborado por Verónica Abacha, Funcionaria adscrita a esta Oficina, en presencia conjunta con el Sr. Jhon Jairo Maldonado, quien se encuentra en calidad de Notario Interino del Estado Miranda. -



La Registradora Principal

[Firma manuscrita]

DRA. ROSA MERCEDES CARREÑO ESCOBAR

[Firma manuscrita]

Verónica Abacha
Planilla Nº 22259
Para el día: 18/03/2005.

REPÚBLICA BOLIVARIANA
DE VENEZUELA

SENIA

F-02 01108679

Nombre del solicitante:

Número de identificación:

Fecha:

Concepto:

1000
Mil Bolívars



REPÚBLICA BOLIVARIANA
DE VENEZUELA

SENIA

F-02 09861861

Nombre del solicitante:

Número de identificación:

Fecha:

Concepto:

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Mil Bolívars



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Mil Bolívars

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REPÚBLICA BOLIVARIANA
DE VENEZUELA

SENIA

F-02 09861785

Nombre del solicitante:

Número de identificación:

Fecha:

Concepto:

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Mil Bolívars



REPÚBLICA BOLIVARIANA
DE VENEZUELA

SENIA

F-02 09861862

Nombre del solicitante:

Número de identificación:

Fecha:

Concepto:

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Mil Bolívars



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REPÚBLICA BOLIVARIANA
DE VENEZUELA

SENIA

F-02 09861863

Nombre del solicitante:

Número de identificación:

Fecha:

Concepto:

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Mil Bolívars



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Mil Bolívars

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REPÚBLICA BOLIVARIANA
DE VENEZUELA

SENIA

F-02 09861864

Nombre del solicitante:

Número de identificación:

Fecha:

Concepto:

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Mil Bolívars



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Mil Bolívars

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REPÚBLICA BOLIVARIANA
DE VENEZUELA

SENIA

F-02 09861865

Nombre del solicitante:

Número de identificación:

Fecha:

Concepto:

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Mil Bolívars



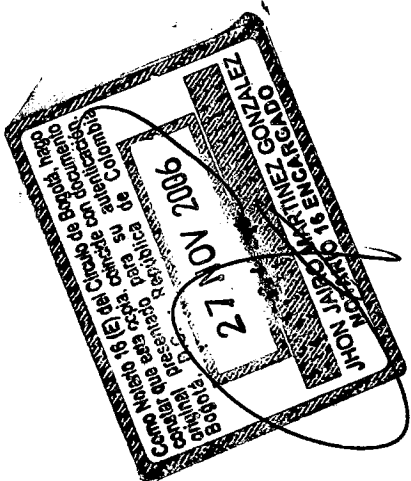
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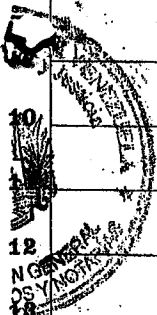




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46	REPUBLICA BOLIVARIANA DE VENEZUELA SENIA F-02 09863088 Nombre del solicitante: Número de identificación: Fecha: Concepto:	1000 Mil Bolivares	46
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52	REPUBLICA BOLIVARIANA DE VENEZUELA SENIA F-02 09863076 Nombre del solicitante: Número de identificación: Fecha: Concepto:	1000 Mil Bolivares	52
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República Bolivariana de Venezuela



MINISTERIO DEL INTERIOR Y JUSTICIA

Se legaliza la firma que antecede de la ciudadana

ROSA CARREÑO ESCOBAR

quien es como se titula, **Registradora Principal del Estado Miranda**

Se advierte que la presente legalización no prejuzga acerca de
ningún otro extremo de fondo ni de forma.

Caracas, **22 MAR 2005**

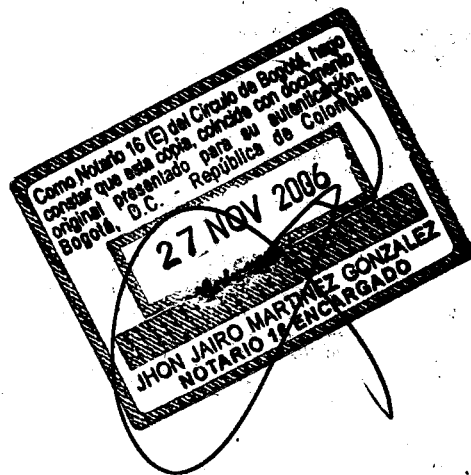
Años 194° y 146°

Por el Ministro,

MARIA CRISTINA BARROSO MATOS

Directora General de Registros y Notarías

Por delegación de firma, según Res. N° 434 del 17-09-2004
publicada en Gaceta Oficial N° 38.025 del 17-09-2004





REPUBLICA BOLIVARIANA DE VENEZUELA
MINISTERIO DE RELACIONES EXTERIORES
DIRECCION GENERAL DE RELACIONES CONSULARES

APOSTILLE

Convention de La Haye del 5 Octobre 1961

1- País: VENEZUELA

El presente documento público :

2- Ha sido suscrito por: MARIA CRISTINA BARROSO MATOS

3- Actuando en su calidad de: DIRECTOR GENERAL DE REGISTROS Y NOTARIAS

4- Llevando el sello/timbre de: MINISTERIO DE INTERIOR Y JUSTICIA

Certificado

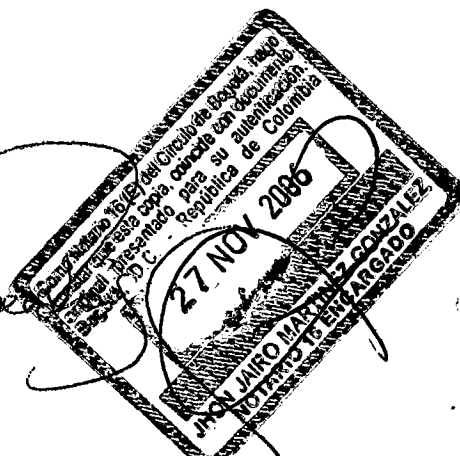
5- En Caracas: 03/31/2005

6- Por el Ministro:

7- N°: 0004170

8- Sello/Timbre

9- Firma



Rebeca Pulg de Escalona
Agregado Juridico
Res. DGRH N°. 175 Del 09/08/01

1722
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REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863094

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863095

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863084

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863085

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 01082419

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 01082425

Nombre del solicitante:

Número de identificación:

Fecha:

Concepto:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863099

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863100

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863089

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863090

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863088

Nombre del solicitante:

Número de identificación:

REPUBLICA BOLIVARIANA
DE VENEZUELA



F-02 09863087

Nombre del solicitante:

Número de identificación:

Fecha:

Concepto:

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Mil Bolívares



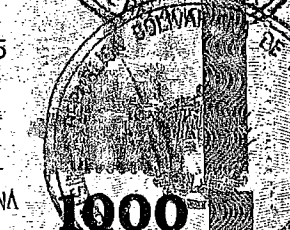
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H-96 N° 10412679

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GAVIRI A

ORGANIZACIÓN ELECTORAL
REGISTRADURÍA NACIONAL DEL ESTADO CIVIL

REGISTRO CIVIL DE DEFUNCIÓN

Indicativo
Serial 5562241

Datos de la oficina de registro

Clase de oficina:	Registraduría	Notaría	X	Consulado	Corregimiento	Insp. de Policía	Código	9795
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COLOMBIA CUNDINAMARCA BOGOTÁ D.C.

NOTARIA 32.

Datos del inscrito

CASTRO DUQUE RAMIRO

Documento de identificación (Clase y número)

C.C. No. 170322 DE BOGOTÁ

Sexo (en Letras)

MASCULINO

Datos de la defunción

Lugar de la Defunción: País - Departamento - Municipio - Corregimiento o/s Inspección de Policía

COLOMBIA CUNDINAMARCA BOGOTÁ D.C.

Fecha de la defunción

Año 2004

Mes 10

Día 30

Hora

04:10 PM

Número de certificado de defunción

A- 2094375.

Lugar que profiere la sentencia

Presunción de muerte

Fecha de la sentencia

Documento presentado

Autorización judicial

Certificado Médico

X

Nombre y cargo del funcionario

ANDRES DIAZ CAMPOS.-

R. M. No. 79982662

Datos del denunciante

Apellidos y nombres completos

EDGAR DAVID REGINO H.

Documentos de identificación (Clase y número)

C.C. No. 15.030.154 DE LORICA/ CORDOBA

Primer testigo

Apellidos y nombres completos

Documentos de identificación (Clase y número)

Firma

Segundo testigo

Apellidos y nombres completos

Documentos de identificación (Clase y número)

Firma

Fecha de inscripción

Año

2004

Mes

11

Día

02

Nombre y firma del funcionario que autoriza

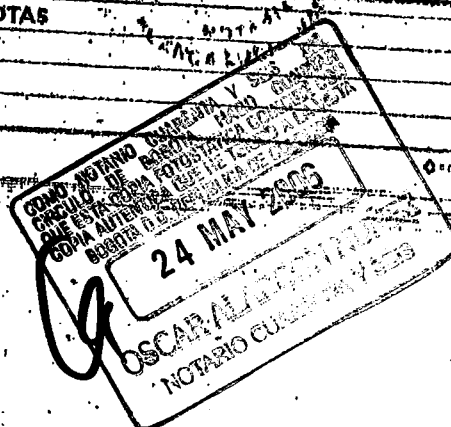
BLANCA LUCIA VALLEJO RESTREPO

NOTARIA 32

PADRES: ALFONSO CASTRO

MERCEDES DUQUE

ESPACIO PARA NOTAS



ORIGINAL PARA LA OFICINA DE REGISTRO

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

Radicación No. 01-35611
Clasificación Internacional (IPC): C 10 L 1/00
Concepto Técnico No. 587

Patente de Invención ☒ Patente de Modelo de Utilidad ☐
 Vía Nacional ☒
 Vía PCT (fase nacional) ☐ Cap. I ☐ Cap. II ☐

Como resultado del examen definitivo, realizado con fundamento en el artículo 48 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

- 1.1. Descripción: Folios 5 a 54 tal como se radicó inicialmente
- 1.2. Reivindicaciones: Folios 62 a 63 tal como se radicó inicialmente
 Folios 208 a 213 tal como se modificó en fecha 10 de enero de 2008
- 1.3. Prioridad: Folios: 72 a 185
 Fecha 5 de mayo de 2000
 País Estados Unidos
 Número 09/565556
- 1.4. Argumentos del solicitante Folios: 204 a 207

2. Modificaciones (artículo 34 D.486 y art. 22 Tratado PCT)

No es posible aceptar las modificaciones realizadas por el solicitante toda vez que amplía el objeto inicial de la solicitud.

De acuerdo con el Artículo 34 de la Decisión 486 "el solicitante de una patente podrá pedir que se modifique la solicitud en cualquier momento del trámite. La modificación no podrá implicar una ampliación de la protección que correspondería a la divulgación contenida en la solicitud inicial." La misma Decisión 486 en su Artículo 51 reza que "el alcance de la protección conferida por la patente estará determinado por el tenor de las reivindicaciones"; y en el artículo 30 se afirma que "las reivindicaciones definirán la materia que se desea proteger mediante la patente".

De acuerdo a lo encontrado en la solicitud original, allí no se contempla la petición de protección del derivado nitro olefínico del ácido oleico. Tampoco se contempla el límite superior del 15% de la fase acuosa en la emulsión.

NO

Además de lo anterior, debe recordarse que según el Artículo 28 "La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla. La descripción de la invención indicará el nombre de la invención e incluirá la siguiente información:... e) una descripción de la mejor manera conocida por el solicitante para ejecutar o llevar a la práctica la invención, utilizando ejemplos y referencias a los dibujos, de ser éstos pertinentes..." Si en la supuesta invención fuera relevante el derivado nitro olefínico del ácido oleico, esto se debería ver reflejado en las mejores formas de llevar a cabo la invención, algo que no sucede. Tampoco hay ejemplos o elementos que permitan afirmar que esto sea así.

Por todo lo anterior, no es posible aceptar las modificaciones hechas por el solicitante.

3. Análisis de la Prioridad

Se aceptan las prioridades anexadas, toda vez que corresponden a la misma materia de la solicitud en estudio

4. Objeto de la invención

- Título de la solicitud *EMULSIÓN DE AGUA EN HIDROCARBUROS*
- Las reivindicaciones 1 a 33 de la solicitud en estudio se refieren a:
 - (1) Una emulsión de agua en hidrocarburo que comprende una fase de agua, una fase de hidrocarburo y a tensioactivo, donde dicha fase de agua está presente en una cantidad mayor que o igual a alrededor de 5% en volumen con respecto al volumen de dicha emulsión, y dicha fase de agua y dicho tensioactivo están presentes a una relación en volumen de dicha fase de agua con respecto a dicho tensioactivo de por lo menos alrededor de 1.
 - (19.-) Un método para elaborar una emulsión de agua en hidrocarburo, que comprende los pasos de: proporcionar una fase de agua; proporcionar una fase de hidrocarburo; proporcionar un tensioactivo; mezclar dicha fase de agua, dicha fase de hidrocarburo y dicho tensioactivo en cantidades suficientes para proporcionar un contenido de agua de por lo menos alrededor de 5% en volumen con respecto a dicha emulsión, y proporcionar una proporción en volumen de dicha fase de agua con respecto a dicho tensioactivo de por lo menos alrededor de 1, donde dicho mezclado se lleva a cabo a una intensidad de mezclado suficiente para formar una emulsión estable de dicha fase de emulsión en agua en dicha fase de hidrocarburo.
- Los anteriores producto y procedimiento buscan elaborar combustibles con mejores propiedades.
- La Clasificación Internacional de Patentes (IPC) para esta solicitud es *C10L1/00*.

5. De la solicitud de Patente (según el caso)

5.1. Reivindicaciones (artículo 30 D 486)

El capítulo reivindicatorio de la solicitud en estudio presenta los siguientes defectos:

- **Palabras ambiguas.** NO se admite el uso de frases y/o palabras que generen ambigüedad o imprecisiones. Por tanto, expresiones como “alrededor”, “baja gravedad”, “sustancialmente libres”, entre otras, NO SON ACEPTABLES. El solicitante, accediendo a las observaciones hechas por esta oficina, está de acuerdo en retirar este tipo de expresiones, por lo que se entenderá que en el capítulo reivindicatorio objeto de estudio, dichas expresiones no existen.
- **Las reivindicaciones de método.** De acuerdo a lo encontrado en el capítulo reivindicatorio, el solicitante pretende que se le proteja un método que no define. El mismo se encuentra redactado de la siguiente forma y presenta los siguientes problemas:

Reivindicación	Problema
Un método para elaborar una emulsión de agua en hidrocarburo, que comprende los pasos de:	
...proporcionar una fase de hidrocarburo;... ... proporcionar un tensioactivo;... ...proporcionar una fase de agua...	Proporcionar, según la Real Academia, es “Disponer y ordenar algo con la debida correspondencia en sus partes”. De lo anterior, el hecho de tomar un paso como “proporcionar un ingrediente” no especifica como se dispone y ordena el ingrediente que el solicitante relaciona y simplemente se relaciona una composición, no un método. Va contra la legislación, toda vez que las reivindicaciones deben definir la materia a proteger, algo que con estas expresiones no sucede.
...mezclar dicha fase de agua, dicha fase de hidrocarburo y dicho tensioactivo en cantidades suficientes...	Este paso es sumamente ambiguo, toda vez que se trata de unir de forma indeterminada la composición tampoco definida antes. Aun más, coloca expresiones ambiguas e inaceptables como “cantidades suficientes”
...para proporcionar un contenido de agua de por lo menos alrededor de 5% en volumen con respecto a dicha emulsión, y proporcionar una proporción (sic) en volumen de dicha fase de agua con respecto a dicho tensioactivo de por lo menos alrededor de 1...	Lo que el solicitante coloca aquí es el objetivo a lograr. Es decir, define lo característico como lo que se quiere alcanzar, algo inadmisibles en una solicitud de patente.
...donde dicho mezclado se lleva a cabo a una intensidad de mezclado suficiente para formar una emulsión estable de dicha fase de emulsión en agua en dicha fase de hidrocarburo...	Es inadmisibles este aparte toda vez que: NO define como es se realiza el mezclado. El afirmar que se realiza con un mezclado suficiente es inaceptable por lo etéreo y ambiguo del mismo. El formar una emulsión estable es también un resultado a alcanzar.

En general, puede decirse que el solicitante no está definiendo ningún método para ser protegido. Un método es una secuencia de pasos perfectamente definidos que permiten alcanzar un fin. El fin es claro, no así los pasos.

Según el solicitante, proporcionar también significa “Poner en aptitud o disposición las cosas, a fin de conseguir lo que se desea” y que con esta definición ya lo hace claro. Esta es una respuesta totalmente desafortunada, toda vez que cualquier técnico encontrará inapropiada la contestación. Poner en aptitud no define absolutamente nada. Poner en aptitud no muestra una etapa técnica. Poner en aptitud es una frase ambigua que da para múltiples interpretaciones. Poner en aptitud no es una frase comúnmente empleada en la técnica pues por sí misma no significa nada. En general son inaceptables las observaciones del solicitante.

En otros apartes de las objeciones hechas por esta oficina, el solicitante da la razón a este despacho.

En general, las reivindicaciones de método no pueden ser ~~estudiadas~~ porque no cumplen con los requisitos de claridad exigidos por la legislación.

ya se
estudiaron.

Por lo anterior, el capítulo reivindicatorio no cumple con el requisito de definición, claridad, concisión o sustento por la descripción de acuerdo al art. 30 de la Decisión 486.y/o art.22 Tratado PCT y por consiguiente. solo se estudiarán de fondo las reivindicaciones 1 a 18.

6. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el estado de la técnica es 5 de mayo de 2000 la cual corresponde a la fecha de presentación de la solicitud prioritaria.
- 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	GB 2217229	Solubilising composition	1989.10.25
D2	WO 9734969	Emulsified fuel and one method for preparing same	1997.09.25
D3	EP 01 57684	Composés oraniques à fonction nitrate utilisables comme additifs pour carburants diesel	1985.10.09
D4	EP 0 475 620	Microemulsion diesel fuel compositions and method of use	1992.03.18
D6	WO 9913031	Emulsion blends	1999.03.18
D7	WO 99 35215	An additive compositions also used as a fuel composition comprising water soluble alcohols	1999.07.15

7. Análisis de patentabilidad (artículo 14 D486)

La presente solicitud quiere que se le proteja una emulsión de agua en hidrocarburo que comprende una fase de agua, una fase de hidrocarburo y un tensioactivo, donde dicha fase de agua está presente en una cantidad mayor que o igual a 5% en volumen con respecto al volumen de dicha emulsión, y dicha fase de agua y dicho tensioactivo están presentes a una relación en volumen de dicha fase de agua con respecto a dicho tensioactivo de por lo menos 1.

	Objeto de la protección
1	Emulsión de agua en hidrocarburo
2	Comprende Fase agua, fase hidrocarburo y tensioactivo.
3	Fase agua, presente en una cantidad mayor o igual a 5% en volumen
4	Relación fase agua/tensioactivo (en volumen) mayor o igual a 1

7.1. Novedad (artículo 16 D486)

7.1.1. Documento D2: WO 9734969

	SOLICITUD COLOMBIANA 01-035611	ANTERIORIDAD D2 DOCUMENTO WO 9734969
1	Emulsión de agua en hidrocarburo	Todo el documento refiere emulsiones de agua en hidrocarburos. Ver por ejemplo el resumen.
2	Comprende Fase agua, fase hidrocarburo y tensioactivo.	Todo el documento refiere una emulsión que tiene una fase agua, una fase hidrocarburo y un surfactante
3	Fase agua, presente en una cantidad mayor o igual a 5% en volumen	En la página 12 se refiere que se recomienda que el agua este en proporción de 0,1 a 50%. El intervalo corresponde plenamente con lo que el solicitante desea proteger.
4	Relación fase agua/tensioactivo (en volumen) mayor o igual a 1	En la página 12 también refiere que el agua preferiblemente se debe encontrar entre 0,1% a 50% y los tensoactivos en un intervalo entre 0,05 a 5%. Es evidente que al proporción de agua/tensoactivo en volumen es mayor o igual a 1

Como se observa, todas las características técnicas de la solicitud colombiana se encuentran anticipadas en el documento WO9734969, por lo que la presente solicitud carece de novedad.

7.1.2. Documento D4 EP 0 475 620

	SOLICITUD COLOMBIANA 01-035611	ANTERIORIDAD D4 Documento EP 0 475 620
1	Emulsión de agua en hidrocarburo	Relaciona una emulsión, más específicamente una microemulsión. Ver resumen.
2	Comprende Fase agua, fase hidrocarburo y tensioactivo.	Comprende una fase de hidrocarburo, una fase agua y un sistema de surfactante. Ver resumen
3	Fase agua, presente en una cantidad mayor o igual a 5% en volumen	Fase agua presente hasta en un 30%. Ver resumen
4	Relación fase agua/tensioactivo (en volumen) mayor o igual a 1	Relación fase agua/surfactante de al menos 2

Obsérvese como todas las características de la solicitud colombiana están contenidas en la anterioridad D4. NO puede hablarse, por consiguiente que exista novedad en la presente solicitud.

7.1.3. Documento D6 WO 9913031

Con esta anterioridad se encuentra que:

	SOLICITUD COLOMBIANA 01-035611	ANTERIORIDAD D6 DOCUMENTO WO 9913031
1	Emulsión de agua en hidrocarburo	Toda la anterioridad se refiere a una emulsión agua-hidrocarburo. Ver resumen
2	Comprende Fase agua, fase hidrocarburo y tensioactivo.	La emulsión comprende una fase hidrocarburo, una fase agua y un surfactante. Ver resumen.
3	Fase agua, presente en una cantidad mayor o igual a 5% en volumen	El agua puede variar en un rango muy amplio, donde se prefiere una relación hidrocarburo/agua desde 90/10 hasta 10/90. Ver página 4.
4	Relación fase agua/tensioactivo (en volumen) mayor o igual a 1	De acuerdo a lo relacionado en la página 5, la cantidad de surfactante mayor a 0.001% y más preferiblemente hasta menos de 5%. Ver folio 5

Nuevamente se halla que la anterioridad revela todo lo que el solicitante pretende que se le proteja. Nuevamente un documento afecta de manera directa la novedad de la presente solicitud.

Como se observa, lo revelado en la solicitud colombiana ya ha sido revelado por documentos anteriores como D2, D4 o D6 de forma independiente. Por lo anterior, se considera que la presente solicitud no posee el requisito de novedad para que se le conceda el privilegio solicitado.

7.2. Nivel inventivo (artículo 18 D486)

7.2.1. Comparando la presente solicitud con el documento D1 se encuentra

	SOLICITUD COLOMBIANA 01-035611	ANTERIORIDAD D1 DOCUMENTO GB 2217229
1	Emulsión de agua en hidrocarburo	Habla principalmente de una solución homogénea de agua y aceite. Habla que son conocidas las emulsiones de agua y aceites o combustibles (hidrocarburos). Página 1.
2	Comprende Fase agua, fase hidrocarburo y tensioactivo.	Comprende una fase agua, una fase aceite y un componente que permite la estabilidad de la solución. La finalidad de este componente es la misma de la de un tensioactivo. Página 3
3	Fase agua, presente en una cantidad mayor o igual a 5% en volumen	Se recomienda que el componente estabilizador sea 10 partes por 10 partes de agua y 100 partes de Diesel. Es decir, el agua debe estar en una proporción de 10/120 equivalente a 8.33%. Es decir mayor a 5% en volumen.
4	Relación fase agua/tensioactivo (en volumen) mayor o igual a 1	Nótese como la relación preferida es 10 partes de estabilizador a 10 partes de agua.

La única diferencia radica en que la anterioridad se enfoca hacia una solución y no una emulsión. Sin embargo, un técnico medio consideraría que cuando se habla de soluciones se podría entender microemulsiones, tal como lo refiere la anterioridad D7 en la página 1. Además de lo dicho, nótese como la D1 da por sentado que existen ya dichas emulsiones y que generan múltiples problemas, por lo que la solución propuesta en dicho documento va mucho más allá de la propuesta de la solicitud colombiana para resolver el mismo problema planteado. Es decir, la anterioridad revela más altura inventiva que la misma solicitud colombiana. Para un experto en la materia, lo revelado en la solicitud colombiana es demasiado obvio partiendo del documento D1.

7.2.2. El documento D3 (EP 01 57684) relaciona un aditivo nitro olefínico que permite mejorar el número de cetano de hidrocarburos diesel. Si bien es cierto que esta anterioridad no señala específicamente el uso del agua, dado lo esbozado por el solicitante y combinando este documento con otro como D2, cualquier persona que conozca del arte encontrará obvio lo enseñado por esta solicitud.

7.2.3. El documento D7 WO 99 35215 enseña

	SOLICITUD COLOMBIANA 01-035611	ANTERIORIDAD D7 DOCUMENTO WO 99 35215
1	Emulsión de agua en hidrocarburo	Relaciona un amplio número de anterioridades que muestran emulsiones agua hidrocarburo. Ver página 6.
2	Comprende Fase agua, fase hidrocarburo y tensioactivo.	Las anterioridades enseñan dichos tres componentes.
3	Fase agua, presente en una cantidad mayor o igual a 5% en volumen	
4	Relación fase agua/tensioactivo (en volumen) mayor o igual a 1	

La anterioridad ha encontrado que aun mejor que las emulsiones con agua, son las emulsiones con alcoholes. Relaciona un buen número de documentos en el que el agua es una de las fases, pero han encontrado que el alcohol posee mejores características que la misma agua. Por tanto, es claro que la anterioridad posee un avance tecnológico mayor al revelado por la solicitud colombiana. Dicho documento D7 enseña que lo revelado por la solicitud colombiana ya ha sido superado. De lo anterior, puede decirse que la presente solicitud carece de la altura inventiva para que se le conceda el privilegio solicitado.

De todo lo anterior, se tiene que la presente solicitud carece de la altura inventiva necesaria para que se le conceda el privilegio solicitado, dado que las composiciones reivindicadas son evidentes para una persona medianamente versada en la materia. Aun más, las anterioridades revelan que la tecnología ha avanzado en grado mayor al revelado por la solicitud colombiana y que esta no representa ningún salto tecnológico.

UK Patent Application GB 2 217 229 A

(43) Date of A publication 25.10.1989

(21) Application No 8809694.6

(22) Date of filing 25.04.1988

(71) Applicants

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(51) INT CL

B01F 17/00 17/22 17/44

(52) UK CL (Edition J)

B1V VF V107 V108 V109 V205

U1S S1359

(56) Documents cited

None

(58) Field of search

UK CL (Edition J) B1V VS VF

INT CL B01F

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(54) Solubilising composition

(57) A solubilising composition allows oil and water, especially diesel oil and water, to be combined as a clear, stable homogeneous solution. The composition comprises appropriate amounts of the following components

- (a) an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and a melting point below -15°C,
(b) a diethanolamide of a higher fatty acid, or a mixture of such diethanolamides, preferably equal parts by volume of lauric diethanolamide and oleic diethanolamide, and
(c) a polyglycol ether of a higher fatty acid, preferably ethoxylated oleic acid, and, optionally also ethylene glycol monobutyl ether. Fuel extenders may also be included in the resulting solution.

SOLUBILISING COMPOSITION

This invention relates to a composition which enables water and oil to be combined into a mixture which behaves as a clear stable homogeneous solution. The composition may be used, for example, in forming stable solutions of fuel oils and water and finds particular use as an additive to diesel fuel oil that has previously been contaminated with water or to diesel fuel oil that might be expected subsequently to suffer from such contamination.

The presence of water in, particularly, fuel oil can cause a number of difficulties. If the water is present as an undesired contaminant, the burning of the resultant fuel is often uneven or, if the fuel is used in an engine, erratic running and stalling often results, together with a serious risk of corrosion. In addition, the presence of water in fuel oils in amounts too small to give rise to such difficulties can still be undesirable as it can produce a lack of clarity or haze which is unappealing to the consumer. On the other hand, there are occasions when it might be desirable to be able deliberately to add water to fuel oils in a stable mixture as an extender and for the known improvements in performance and cleaner exhaust emission that can result in, for example, engines using diesel fuel.

A large number of attempts have been made to deal with these problems by attempting to create stable emulsions of the diesel or other fuel oil with water. Such attempts, even with proprietary brands of additive (diesel fuel improvers), have not been wholly successful because long-term stability of the resulting mix cannot be achieved in practice. As the emulsions or suspensions formed with the addition of such additives break down, problems of poor engine

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running, even stalling, and corrosion of system components (including biologically aggravated corrosion) arise. Stability problems have been found to be particularly acute with the higher fraction distillate hydrocarbon fuels (such as gasolene, kerosene and normal diesel fuels) in which separation of the oil and water components often occurs in a very short period of time. Where biocides are added to the emulsion to combat biochemically aggravated corrosion, this adds more complications to the already difficult task of attempting to formulate fuel additives for the stable mixing of oil and water.

The present invention seeks to avoid the above mentioned problems and to provide additives which allow the formation of oil-water mixtures which are true solutions or behave as such. The term "solution" herein thus includes any mixtures which are clear, homogeneous and have substantially the same stability as solutions.

The present invention accordingly provides a composition for combining oil and water as a stable solution which comprises (a) an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and a melting point below -15°C , (b) a diethanolamide of a higher fatty acid, or a mixture of such diethanolamides and (c) a polyglycol ether of a higher fatty acid.

The components of the composition are appropriately mixed together (with the alcohol ethoxylate as the major component) in amounts which would allow a solution to be formed on addition to the intended oil and water mixture. The mentioned higher fatty acids include the normal emulsifier-forming acids, of which lauric and oleic acid are particularly preferred.

Particularly preferred compositions of the invention comprise the following components

- (1) 48 parts by volume of an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and a melting point below -15°C ,
- (2) 3-8 parts by volume of lauric diethanolamide,
- (3) 3-8 parts by volume of oleic diethanolamide,
- (4) 1.5-4 parts by volume of a polyglycol ether of a higher fatty acid, e.g. ethoxylated oleic acid,

the parts by volume in each case being relative to the total volume of the composition.

In an alternative embodiment components (2) and (3) are replaced by 6 to 16 parts by volume of either lauric diethanolamine or oleic diethanolamine alone.

The composition according to the invention preferably also includes 0.25 to 1 part by volume of ethylene glycol monobutyl ether as an extra component. The presence of this extra component is particularly useful in dealing with mixtures of water and lighter fraction oils.

The present invention further provides a method of forming a stable solution of an oil and water mixture comprising adding to the oil and water mixture a composition of the invention in an amount sufficient to provide a clear stable solution on mixing, and such a solution when so produced.

The number of parts by volume of each component in the composition is selected so as to allow for the

formation of a stable solution of the intended oil and water mixture. The exact amounts of each component of the composition required to give a solution of the intended oil-water combination may easily be found by simple experiment.

As an example, if a 10 parts by water of water in 100 parts by volume of normal diesel oil is to be treated, an appropriate composition would comprise 48 parts of component (1), 8 parts each of components (2) and (3), four parts of component (4) and 1 part of the ethylene glycol monobutyl ether. Where there is a lower amount of water present, lesser proportions of components (2) to (4) would normally be present in the composition. For example, if 1 part by volume of water in 100 parts by volume of diesel is to be treated, an appropriate composition would comprise 48 parts of component (1), 3 parts of components (2) and (3), 1.5 parts of component (4) and 0.25 parts of the ethylene glycol monobutyl ether.

The minimum quantity of composition to be added would normally be expected to be between 5 and 15 parts by volume relative to the volume of the oil water mixture to be treated, but the exact amount may be found by gradually mixing in the composition until a clear solution is formed. Thus, for example, 10-12 parts of the agent (but preferably 16 parts for the best effect) are sufficient to treat the 10 parts water : 100 parts diesel mixture already mentioned, whereas 6 parts by volume per 100 parts of mixture are suitable for treating the 1 part water : 100 parts diesel mixture. The addition of too low a quantity of composition to the oil and water mixture (as for example only 2 parts of composition to the first mentioned water: diesel mixture) is to be avoided as it will result in just an emulsion being formed instead of a solution.

The components of the composition are all readily available commercially. Suitable alcohol ethoxylates of component(1) are for example "Dobanol 91/2.5" (Trade Mark of Shell Chemicals) and "Synperonic 91/2.5" or "Synperonic A 3" (Trade Marks of I.C.I. Plc.). "Texofor M-6" (Trade Mark of ABM.Limited) is suitable as the polyglycol ether of higher fatty acids of component(4).

Particularly preferred ethoxylates of component (1) are those based on C₉ and C₁₁ alcohols mixtures, more especially mixtures also including alcohols having chains with even numbers of carbon atoms.

"Dobanol 91/2.5" is such an ethoxylate obtained by the addition of 2.5 moles of ethylene oxide per mole of Dobanol 91 (a mixture of C₉, C₁₀ and C₁₁ alcohols).

The less highly preferred "Synperonic 91" range is manufactured by the base catalysed ethoxylation of Synprol 91 - a fully saturated synthetic primary alcohol which contains only C₉ and C₁₁ alkyl chains and typically consists of 50% w/w linear alcohols with the remainder being monobranched and predominantly the 2-methyl isomer.

The composition of the present invention not only allows ready mixing of fuel oils and water but also allows the addition of further substances as fuel extenders in the oil-water solution. Thus, for example, animal and vegetable oils, even including tallow and butter, may be added successfully to diesel oil and water to form a clear solution on addition of the composition of this invention.

Other extenders which contain water or are hygroscopic, such as alcohols, may also be

successfully added to fuel oils to form permanent mixtures with the fuel oil. Previous attempts to extend fuel with alcohols, for example, have not been wholly successful because of phase separation and subsequent burning out of valves in the engine by the resulting pure alcohol component.

The compositions of the present invention allow the formation of stable solutions which show no sign of breaking down after extended periods of time, in contrast with the emulsions formed with prior art additives. Thus oil and water mixtures incorporating compositions of the invention have formed clear solutions showing no sign of separation of the components over periods of as long as three years.

The uses of solubilising compositions are by no means restricted to these uses but include numerous other applications such as oil recovery, the safe cleansing under pressure of oil tanks (conventional low-flash point solvents being unnecessary) and as additives to jet fuel. However yet further applications will readily occur to the man skilled in the art.

The following examples illustrate the formation of compositions of the invention and their use for the formation of stable solutions of water and oil and also show that such solutions (in contrast to emulsions formed with conventional additives) have no significant corrosive effect on the various materials employed as fuel system and engine components.

Example 1

A composition suitable for combining 100 parts of diesel with 10 parts of water by volume was prepared by adding together the following surfactants in the volume proportions stated:

240 parts Dobanol 91/2.5
40 parts lauric diethanolamide
40 parts oleic diethanol amide
20 parts ethoxylated oleic acid (e.g. Texofor M6)
5 parts ethylene glycol monobutyl ether

The surfactants were mixed vigorously together to form a homogeneous solution.

The following Example shows the use of this composition for forming a solution of a 10:1 by volume mix of diesel and water.

Example 2

10 ml of water was added to 100 ml of diesel in a clear glass container. The composition of Example 1 was introduced into the resulting diesel-water mixture using a syringe, or an accurately calibrated measuring cylinder capable of holding 15 to 20 ml, and the mixture was stirred slowly until a clear homogeneous solution was created. A good degree of clarity was achieved after some 10 to 12 ml of the composition of Example 1 had been introduced. The remaining bloom was removed, when desired, by the further addition of up to 4 ml of the composition.

The composition according to the invention may equally be formed in situ when forming the oil-water solution, as will be seen from the following Examples 3 and 4.

Example 3

A clear solution of diesel oil and water having a volume ratio of 10:1 was formed by combining 100 ml diesel oil and 10 ml water in a suitable transparent glass container and thereafter adding thereto a mixture of 6 ml "Dobanol 91/2.5" and 2 ml oleic diethanolamide and stirring slightly. The solution resulting cleared to a smokey haze. Next a mixture of 1 ml ethoxylated oleic acid "Texofor M6" and 0.25 ethylene glycol monobutyl ether was stirred in.

In a second step, a mixture of "Dobanol 91/2.5" and oleic diethanolamide in a volume ratio of 3:1 continued to be added, stirring gently, until a clear solution was achieved. Not more than 6 ml of "Dobanol 91/2.5" and 2 ml of oleic diethanolamide provided by this latter mixture was normally required - the precise amount depending on their age and quality.

As an alternative, the oleic diethanol amide could be replaced, in part or in whole, by lauric diethanolamide.

Example 4

A clear solution of diesel oil and water having a volume ratio of 100:1 was formed in an identical manner to that of Example 3 except that 3 ml "Dobanol 91/2.5", 0.3 ml oleic diethanolamide, 0.15 ml "Texofor M6" and a few drops of ethylene glycol monobutyl ether were employed in the first step and a mixture of "Dobanol 91/2.5" and lauric diethanolamide in a volume ratio of about 6:1 normally providing not more than 2 ml of "Dobanol 91/2.5" and 0.3 ml of lauric diethanolamide was employed in the second step.

The of amounts of solubilising composition which need to be added to particular oil and water mixtures to obtain a solution may be determined in a similar manner to that shown in the following Example.

Example 5

3 ml of water were mixed with 30 ml of diesel oil. Thereafter 1, 2, 3, 4, 5 and 6 ml portion of the composition of Example 1 were added to separate sample of the oil:water mixture. The results shown in Table 1 were obtained.

Table 1

Content of composition of Example 1 Effect on the diesel oil:water mixture

1 ml	A white substance resembling white gloss paint formed which settled to the bottom of the container. The bulk of the liquid was a semi-clear red.
2 ml	An emulsion with an appearance similar to creme shampoo was formed. This emulsion appeared relatively stable. After 3 weeks it had, however, separated into four layers.
3ml	A reddish solution with a blue haze to it was formed. Even after 3 weeks this solution remained stable with no visible separate occurring.
4ml	A clear diesel-red solution was obtained with no haze and no separation of fluid occurring.

Table 1 (cont'd.)

Content of composition of Example 1	Effect on the diesel oil:water mixture
5 ml	No further improvement could be made
6 ml	to the solution containing 4 ml of the composition of Example 1. A similar clear diesel-red solution was obtained using these quantities of the composition although these solutions turned very slightly cloudy after standing for 3 weeks.

The foregoing Table thus shows that the addition of just 9% by volume of the composition is sufficient to allow a solution of the 10:1 diesel:water mixture to be formed. The addition of amounts of composition in excess of 12% by volume may be seen to give no further benefit.

The effectiveness of compositions of the invention as compared with that of proprietary diesel fuel improvers which are claimed to absorb moisture in vehicle fuel systems is shown in the following Example.

Example 6

The composition of Example 1 and other proprietary diesel fuel improvers were compared by adding 10% water to the composition and improvers and vigorously shaking the samples to distribute the water. The specimens were then left to stand.

When the water was added to the composition of Example 1 a reaction was seen to occur immediately. The other diesel fuel improvers, although appearing slightly cloudy when vigorously shaken, very quickly separated into two layers. The composition of Example 1 remained a homogeneous clear pale yellow

liquid even after standing. A piece of mild steel was inserted into each sample. Although this gave no reaction with the mixture of water and the composition of the Example, considerable corrosion occurred in the steel in the other fuel improver samples showing the presence of a separate water phase.

Further investigation showed that the diesel fuel improvers failed to absorb even 0.5% water in diesel.

The compositions of the invention (in pure form and in an oil:water solution) show slight or no corrosive effect on the standard component materials of engines and fuels systems, as may be seen from the following Examples 7 and 8.

Example 7

Samples of the test materials listed in the following Table were each carefully cleaned using emery cloth in the case of metallic samples and tissue in the case of non-metallic samples. A separate jar was provided for each sample in the case of each of the three fluids. The respective jars were then filled with test fluids which were (a) untreated diesel oil, (b) the pure composition of Example 1 and (c) a solution consisting of 30 ml of diesel oil, 3 ml of water and 4 ml of the composition of Example 1 (referred to in Table 2 as "Solution-S1"). Next cleaned samples were immersed in the test fluid in the jars which were left undisturbed at room temperature (20°C) for two months. Table 2 records the visual changes which were noted after this time.

236

Table 2

Test Material	Rubber	Bundy tube	Reinforced nylon tubing	Copper	Brass	Dural aluminium alloy	Cold-drawn steel tube	Structural steel
Effect on Fluid (1) Untreated Diesel Oil (2) Solution S1 (3) Pure Additive of Example 1	-	-	-	separation into three layers discoloured (pale green)	discoloured (dark black haze at base) green wisps at top of sample	-	-	-
Effect on Test Material (1) Untreated Diesel Oil (2) Solution S1 (3) Pure Additive of Example 1	-	-	Colour of fluid slightly opaque	-	blackened	slight gold tint	-	slightly tinted brown
	size expanded	-	Colour of fluid	etched dull pink	"	-	-	"
	-	-						

- = no visible change

Separate tests show the rubber sample to increase in weight on contact even with untreated diesel. Hence the type of rubber tested would obviously be unreliable in diesel systems.

The noted reaction on copper and brass may be only a surface coating but, in any case, it is anticipated that neutralisation or at least a reduction in the alkalinity in other forms of the solubilising composition may reduce or remove this effect.

Example 8

Since tank corrosion is usually initiated at the interface between the liquid and the air above, a test was set up to simulate conditions in a fuel tank.

Narrow strips of mild steel were placed in bottles half-filled with test fluids, the solution of Example 7, untreated diesel, water and in addition, an emulsion formed by adding only 2 parts of the composition of Example 1 to 30 parts of diesel and 3 parts of water. One set of these four bottles was left undisturbed, another was inverted once and then left undisturbed and a third set was inverted daily. The tops of the bottles were loosened to allow air into the bottles and the effects of corrosion were observed.

The only liquid sample to show any sign of corroding the steel in any of the sets of bottles was water. The emulsion and solution both left the steel perfectly clean, as did the untreated diesel.

The following Example shows that compositions of the invention when added to diesel fuel allow the fuel to be used effectively in engines with possible cost saving from the presence of water or other additives as fuel extenders.

10/1/58
1/58
1/58

Example 9

A series of tests were conducted on a "Ricardo E6" (Trade Mark) single cylinder four stroke compression-ignition engine in which the compression ratio was set at approximately 22 : 1 and the injection timing was set at 35° before T.D.C. (except for two spot checks of the effects of varying this, which were made in one test at 25 00 rev/min).

A first set of tests was carried out at a constant engine speed of 1500 rev/min to obtain engine torque as a function of pump rack (i.e. throttle) setting. Except in the region of full throttle opening the torque output at a given throttle setting (and hence fuel consumption rate) from a normal diesel fuel was found to be higher than when the composition of Example 1 was added to take a 10:1 diesel:water mix into a fuel solution. Expressed another way - to obtain a given torque, and hence power output, with the fuel solution it was found to be necessary on this test engine, at 1500 rev/min, at low powers, to increase the throttle opening slightly, to compensate for there being less diesel fuel in the total liquid flowrate.

Next a second set of tests enabled performance curves of net load or torque at nearly full throttle to be generated as a function of engine speed in the range 800 - 3000 rev/min by adjusting the load on the torque dynamometer whilst maintaining a constant throttle rack setting.

At engine speeds below about 1600 rev/min the above-mentioned solution provided a greater power output than normal uncontaminated diesel. From 1600 rev/min up to around 2100 rev/min the position was reversed with normal diesel apparently being slightly better, and above this speed normal diesel fuel was considerably better.

However, these tests were conducted at a constant injection timing. Spot tests at 2500 rev/min with both normal diesel fuel and the solution of the diesel:water mix indicated that performance would be improved by advancing the injection timing and also that a greater improvement occurred with the fuel solution. If injection timing could be optimised over the speed range it is anticipated that the benefits of improved performance at this throttle setting should be extended to a speed rather higher than 1600 rev/min.

This Example thus shows that under certain conditions (at least) or with certain types of engines diesel fuel which has been contaminated with 10% tap water and to which the composition of the invention is added to form a solution yields essentially the same, and perhaps slightly improved, power output as a normal uncontaminated diesel fuel oil. It has also been found to be possible to run an engine on diesel fuel oil to which had been added 18% by volume of butter and sufficient of the composition of Example 1 to form a solution.

CLAIMS

1. A composition for combining oil and water as a stable solution which comprises
 - (a) an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and melting point below -15°C ,
 - (b) a diethanolamide of a higher fatty acid, or a mixture of such diethanolamides, and
 - (c) a polyglycol ether of a higher fatty acid.
2. A composition according to claim 1, which comprises the following components

- (1) 48 parts by volume of an oil-soluble grade of alcohol ethoxylate having a hydroxyl number greater than 160 and a melting point below -15°C ,
- (2) 3-8 parts by volume of lauric diethanolamide,
- (3) 3-8 parts by volume of oleic diethanolamide,
- (4) 1.5-4 parts by volume of a polyglycol ether of a higher fatty acid,

the parts by volume in each case being relative to the total volume of the composition.

3. A composition according to claim 2, additionally comprising 0.25 to 1 part by volume, relative to the total volume of the composition, of ethylene glycol monobutyl ether.

4. A composition according to claim 3 for combining 10 parts by volume of water in 100 parts by volume of diesel oil, comprising 48 parts by volume of the ethoxylate of component (1), 8 parts by volume of

each of the diethanolamides of components (2) and (3), 4 parts by volume of the ether of component (4) and 1 part by volume of ethylene glycol monobutyl ether, the parts by volume being relative to the total volume of the composition.

5. A composition according to claim 3 for combining 1 part by volume of water in 100 parts by volume of diesel oil, comprising 48 parts by volume of the ethoxylate of component (1), 3 parts by volume of each of the diethanolamides of components (2) and (3), 1.5 parts by volume of the ether of component (4) and 0.25 parts by volume of ethylene glycol monobutyl ether, the parts by volume being relative to the total volume of the composition.

6. A method of forming a solution of a mixture of oil and water comprising adding a composition according to any of claims 1 to 5, to the oil and water mixture in an amount sufficient to provide a clear solution on mixing.

7. A method according to claim 6, in which a composition according to claim 3 is added to a mixture of 10 parts by volume of water and 100 parts by volume of diesel oil in an amount of 14 parts by volume relative to the oil and water mixture.

8. A method according to claim 6, in which a composition according to claim 5 is added to a mixture of 1 part by volume of water and 100 parts by volume of diesel oil in an amount of 6 parts by volume relative to the oil and water mixture.

9. A solution whenever produced by the process of any of claims 6 to 8.

10. A solution according to claim 9, additionally containing a fuel extender.

11. A solution according to claim 10, in which the fuel extender is ethanol, tallow, butter or a vegetable oil.

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(54) Titre: COMBUSTIBLE EMULSIONNE ET L'UN DE SES PROCÉDES D'OBTENTION

(57) Abstract

Novel fuels consisting of emulsions of water in hydrocarbons (e.g. diesel fuel) are disclosed. The underlying problem is that of providing fuels (e.g. for engines) consisting of stable, non-polluting, low-cost water/hydrocarbon emulsions. The solution provided consists of an emulsion of water in at least one hydrocarbon, said emulsion including a surfactant system that essentially comprises a sorbitan sesquiolate (I), a polyethylene glycol monooleate (II) and a nonylphenol ethoxylate (III), characterised in that the average droplet size of the aqueous dispersed phase is no higher than 1 µm, with a standard deviation of 1 µm, and in that the emulsifying system composition is I:II:III → 3:2:1 parts by weight. The surfactant system has an HLB from 6 to 8. A method for preparing said emulsions is also disclosed. The fuels may be used as diesel oil, petrol, kerosene or fuel oil optionally emulsified with water.

(57) Abrégé

La présente invention concerne des nouveaux combustibles constitués par des émulsions d'eau dans des hydrocarbures (gazole e.g.). La problématique sous-tendant l'invention est la fourniture de combustibles (e.g. carburants) formés par des émulsions eau/hydrocarbures stables non polluants et économiques. La solution proposée consiste en une émulsion d'eau dans au moins un hydrocarbure, ladite émulsion comprenant un système tensioactif comportant essentiellement: un sesquiolate de sorbitan (I), un monooleate de polyéthylène glycol (II), un éthoxylate de nonylphénol (III), caractérisée en ce que la taille moyenne des gouttelettes de phase dispersée aqueuse est inférieure ou égale à 1 µm, avec un écart type de 1 µm, et en ce que la composition de système émulsifiant est la suivante, I : II : III → 3 : 2 : 1 parties en poids. Le système tensioactif présente une HLB comprise entre 6 et 8. L'invention a également pour objet un procédé permettant d'obtenir ces émulsions. Application: gazoles, essences, kérosènes, mazouts, fuels émulsionnés avec de l'eau.

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COMBUSTIBLE EMULSIONNE ET L'UN DE SES PROCEDES D'OBTENTION

DOMAINE TECHNIQUE :

5 Le domaine de la présente invention est celui des compositions combustibles, en particulier, des carburants destinés à être utilisés dans les moteurs thermiques. Plus précisément, les combustibles envisagés dans le cadre de l'invention contiennent majoritairement des hydrocarbures liquides et notamment :

- ceux d'origine minérale tels que les dérivés de pétrole du type essences, gazoles, kérosènes, mazouts et/ou tels que les dérivés de charbon ou du gaz (carburants de synthèse).
- ceux d'origine végétale tels que les huiles végétales esterifiées ou non,
- et leurs mélanges.

15 La présente invention vise plus spécifiquement de nouvelles compositions de combustibles constituées par des émulsions d'eau dans au moins un hydrocarbure et généralement dans un mélange d'hydrocarbures, comme par exemple celui qui compose le gazole. Il va donc être question dans le présent exposé d'émulsions stabilisées *eau/hydrocarbures*, comprenant des tensioactifs propres à permettre l'émulsification et la stabilisation de telles émulsions.

20 La présente invention a également pour objet un procédé d'obtention de combustibles (e.g. carburants) émulsionnés *eau/hydrocarbures* associés à un ou plusieurs tensioactifs.

ART ANTERIEUR :

25 La présente invention s'inscrit dans la démarche, depuis longtemps en vogue, de mise au point de compositions de combustibles notamment de carburants comprenant des produits de substitution des dérivés de pétrole, dans des soucis d'économie et de limitation de la pollution.

30 L'eau est très vite apparue comme un additif ou un substituant partiel intéressant de l'essence ou du gazole. L'eau est en effet un liquide peu onéreux et non toxique, qui s'est montré apte à diminuer la consommation en carburant, de même que l'émission de polluants visibles ou non.

35 Malgré tous ces avantages présumés, aucun carburant *eau/hydrocarbures* n'a jusqu'alors été utilisé industriellement, à grande échelle, dans des applications concrètes, en raison de difficultés rédhibitoires de mise en oeuvre et d'utilisation.

Selon une première approche, il a été envisagé de prévoir le stockage séparé d'eau et de carburant sur le véhicule et leur mélange au moment de l'utilisation. Cette approche nécessite l'implantation à bord du véhicule d'un dispositif complexe et sophistiqué de mélange et de dosage spécifiques. Le coût, l'encombrement et la fragilité de tels dispositifs sont apparus comme étant totalement dissuasifs pour le développement de cette approche.

5 La deuxième approche appréhendable consiste à mettre en oeuvre des mélanges tout prêts d'eau et de carburant, mais cela était sans compter avec les problèmes considérables de stabilité au stockage de tels mélanges dans des domaines de température variant de - 20° C à - 70° C, et de stabilité dans des conditions d'utilisation de l'émulsion dans un réservoir.

10 Il existe ainsi de multiples propositions techniques infructueuses, qui visaient, en vain, à fournir des carburants émulsionnés comprenant de l'eau et, plus généralement, de nouveaux carburants non polluants, et entraînant une faible consommation.

15 A titre d'illustration d'un tel état de la technique, on peut citer la demande de brevet français N° 2 470 153 qui divulgue un carburant émulsionné, comprenant des hydrocarbures, de l'eau, un alcool (méthanol, éthanol) et un système émulsifiant formé par du monooléate de sorbitan et par du nonylphénol éthoxylé. La concentration du système émulsifiant dans l'émulsion est comprise entre 3 et 10 % en volume. La présence indispensable d'alcool dans cette émulsion, constitue un élément extrêmement pénalisant, notamment au regard de l'économie et des performances moteurs susceptibles d'être obtenues avec cette émulsion. En outre, il y a lieu de noter que la stabilité de cette émulsion *eau-alcool/hydrocarbure* n'est pas des plus probantes. En effet, au bout de 72 heures de stockage de l'émulsion, ce qui correspond à une durée réaliste de non-utilisation d'un véhicule fonctionnant avec ce carburant, on assiste à un début de séparation de phases (déphasage/démixtion) entre les hydrocarbures et le mélange hydroalcoolique. Les hydrocarbures déphasés (séparés) au terme de cette durée peuvent représenter jusqu'à 3 % en volume de l'émulsion. Il est aisé d'imaginer qu'après quelques jours de stockage, le déphasage de cette émulsion selon la demande N° 2 470 153 est suffisamment important pour devenir rédhibitoire au fonctionnement, dans des conditions normales d'application.

25 On connaît par ailleurs au travers du brevet US N° 4 877 414 un carburant émulsionné comportant un certain nombre d'additifs, dont un système émulsifiant formé par du sesquioléate de sorbitan, du mono-oléate de sorbitan et de l'éther de polyoxyéthylène (6 OE) de dodécylalcool. De manière préférée selon ce brevet, la

241

concentration totale de tous les additifs est d'environ 2,1 %. Hormis le système émulsifiant, les autres additifs susceptibles d'être employés peuvent être : une mono- α -oléfine (décène-1), le méthoxyméthanol, le toluène, un alkyle benzène et l'hydroxyde de calcium. Cette formulation est extrêmement complexe, ne serait-ce que par le nombre d'additifs mis en oeuvre. Elle est en outre relativement onéreuse. Enfin, le carburant émulsionné selon ce brevet souffre lui-aussi d'un manque de stabilité, en particulier à basse température. La Demanderesse a d'ailleurs pu mettre cela clairement en évidence en reproduisant l'exemple préféré de mise en oeuvre du carburant émulsionné selon ce brevet US. Il s'est avéré que l'émulsion se sépare (déphase) en une heure. Le phénomène est encore accentué à basse température inférieure à 5° C. On ose alors à peine imaginer, ce qui pourrait se produire dans des réservoirs de véhicule contenant cette émulsion et placés dans des conditions hivernales réelles d'utilisation.

L'abrégé du brevet japonais N° 77-69 909 donné dans le chemical abstract 87:138 513 z, concerne un carburant émulsionné (kérosène : eau) comprenant du sesquioléate de sorbitan et de l'éther de polyéthylène glycol de nonylphénol, à titre d'émulsifiants. La taille des gouttelettes de phase dispersée aqueuse est $\leq 20 \mu$ et en moyenne de l'ordre de 10μ . Cette proposition technique ne permet pas elle non plus, de satisfaire convenablement aux objectifs de stabilité physicochimiques, de limitation de la pollution, d'économie et de réduction de la consommation en carburant. Cet enseignement technique ne peut donc être d'aucun secours pour un homme du métier se plaçant dans la démarche prospective de l'invention.

Un autre chemical abstract, N° 101 : 57 568 z, résumant le brevet brésilien n° 82 4 947, vise un combustible émulsionné comprenant des hydrocarbures constitués par des dérivés de pétrole extrêmement visqueux et lourds, de l'eau, de l'éthanol et un émulsifiant constitué par du nonylphénol éthoxylé. Ce combustible émulsionné est destiné à être utilisé dans les fours, les brûleurs à mazout conventionnels. Ce combustible ne saurait répondre aux spécifications attendues de performances de combustion, de limitation des polluants et de faible consommation. En outre, la stabilité physicochimique de cette émulsion n'est pas bonne.

La demande de brevet internationale PCT WO-93/18117, au nom de la Demanderesse, décrit des combustibles émulsionnés que la présente invention se propose de perfectionner.

Ces combustibles émulsionnés, qui peuvent être des carburants, comprennent des quantités spécifiques d'hydrocarbures et un ensemble d'additifs en quantité mineure dont notamment un système émulsifiant comprenant de l'oléate de sorbitan, du

polyalkylène glycol et de l'éthoxylate d'alkylphénol. La phase dispersée de ces combustibles émulsionnés est constituée par de l'eau présente à hauteur de 5 à 35 % en poids tandis que les additifs sont présents à hauteur de 0,1 à 1,5 % en poids.

Les plages de concentration en oléate de sorbitan, en polyalkylène glycol et en éthoxylate d'alkylphénol sont, respectivement (en % en poids), de 0,20-0,26/0,20-0,25/0,20-0,27. Toute la demande de brevet fait état de la mise en oeuvre de quantités égales de ces trois additifs principaux : 1/1/1.

Les performances de ces combustibles émulsionnés connus, en terme de stabilité, de réduction des polluants visibles et invisibles, de réduction de la consommation et d'économie, sont tout à fait perfectibles. En particulier, la recherche et développement sur ces carburants émulsionnés a permis de révéler que des améliorations en terme de coût et de stabilité de l'émulsion étaient souhaitables, notamment dans des conditions réelles d'utilisation sur véhicule.

Il ressort de cette revue de l'art antérieur qu'il existe un besoin insatisfait en un combustible émulsionné qui soit physicochimiquement stable (pas de déphasage), peu polluant, économique et réducteur de consommation.

Fort de ce constat, la Demanderesse s'est donc fixée un certain nombre d'objectifs qui vont être énumérés ci-après.

L'un des objectifs essentiel de la présente invention est de pallier cette lacune en fournissant un combustible émulsionné, en particulier un carburant, formé par une émulsion stable eau/hydrocarbures, qui reste parfaitement homogène sur de longues périodes de temps, aussi bien dans des réservoirs de stockage que dans des éléments des circuits constituant les dispositifs de combustion, dans lesquels lesdits combustibles sont susceptibles d'être utilisés.

Un autre objectif essentiel de la présente invention est de fournir de nouveaux carburants émulsionnés perfectionnés procurant de bons résultats en matière de réduction de la consommation de combustibles et de réduction de l'émission de polluants visibles que sont les fumées et les particules solides et de polluants invisibles gazeux tels que CO, NO_x et/ou SO_x, hydrocarbures imbrûlés et CO₂.

Un autre objectif essentiel de la présente invention est de fournir de nouveaux combustibles émulsionnés qui soient d'un prix de revient faible, de manière à ne pas annihiler le gain procuré par le remplacement partiel d'hydrocarbures coûteux par de l'eau.

Un autre objectif de la présente invention est de fournir un procédé de préparation de combustibles émulsionnés stables, non polluants et économiques,

lequel procédé se devant d'être lui-aussi peu onéreux et par ailleurs facile à mettre en oeuvre, sans protocole opératoire et dispositif sophistiqués.

Dans un tel contexte, la Demanderesse a poursuivi son effort inventif et a mis au point de nouveaux combustibles émulsionnés perfectionnés, dont l'originalité est,

d'une part, de présenter une phase dispersée aqueuse, constituée de gouttelettes de taille réduite dotées d'un film interfacial permettant de parer au phénomène de coalescence. Il est en outre essentiel pour la stabilité de l'émulsion que la distribution de taille des gouttelettes d'eau soit aussi fine que possible,

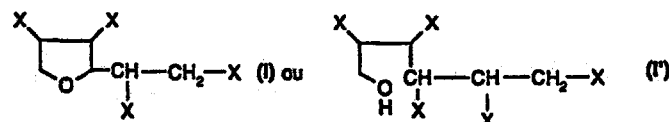
et d'autre part, de sélectionner une composition du système émulsifiant concourant à l'obtention des spécifications de stabilité, de taille et de distribution de taille gouttelettes de la phase aqueuse dans la phase gazeuse.

EXPOSE SUCCINCT DE L'INVENTION :

D'où il s'ensuit que la présente invention concerne un combustible émulsionné perfectionné, constitué par une émulsion d'eau dans au moins un hydrocarbure, ledit combustible étant caractérisé

→ en ce que cette émulsion comporte un système émulsifiant comprenant :

Δ (I) au moins un ester de sorbitol de formule générale :

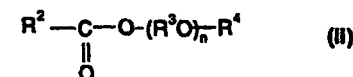


dans laquelle :

- les radicaux X sont identiques ou différents entre eux et correspondent chacun à : OH, R¹COO- avec R¹ représentant un radical hydrocarboné aliphatique, saturé ou insaturé, linéaire ou ramifié, éventuellement substitué par des hydroxyles et ayant de 7 à 22 atomes de carbone, R¹ étant de préférence un reste acide gras privé d'un carboxyle terminal,

cet ester (I) présentant une HLB comprise entre 1 et 9 ;

Δ (II) au moins un ester d'acide gras de formule générale :



dans laquelle :

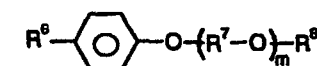
- R² représente un radical hydrocarboné aliphatique, saturé ou insaturé, linéaire ou ramifié, éventuellement substitué par des fonctions hydroxyles et ayant de 7 à 22 atomes de carbone, R² étant de préférence un reste acide gras privé d'un carboxyle terminal,
- R³ étant un alkylène linéaire ou ramifié en C₁-C₁₀, de préférence en C₂-C₃,
- n est un nombre entier supérieur ou égal à 6 de préférence compris entre 6 et 30,
- R⁴ correspond à : H, alkyle linéaire ou ramifié en C₁-C₁₀,



avec R³ répondant à la même définition que celle donnée supra pour R² ;

cet ester (II) ayant de préférence une HLB supérieure ou égale à 9 ;

Δ (III) au moins un alkylphénolpolyalcoxyolé de formule générale :



dans laquelle :

- R⁶ représente un alkyle linéaire ou ramifié en C₁-C₂₀, de préférence en C₇-C₂₀ ;
 - m est un nombre entier supérieur ou égal à 8, de préférence compris entre 8 et 15,
 - R⁷ et R⁸ répondent respectivement aux mêmes définitions que celles données supra pour R³ et R⁴ de la formule (II),
- cet ester (III) ayant de préférence une HLB comprise entre 10 et 15 ;

→ en ce que ce système émulsifiant a une HLB globale comprise entre 6 et 8, de préférence entre 6,5 et 7,5.

→ et en ce que l'émulsion est réalisée de telle sorte que la taille moyenne des gouttelettes de phase dispersée aqueuse soit inférieure ou égale à 3 µm, de préférence à 2 µm et plus préférentiellement encore à 1 µm, avec un écart-type inférieur à 1 µm.

5 Ces caractéristiques avantageuses et innovantes portant :

- sur le profil dimensionnel des gouttelettes de phase aqueuse
- et sur la sélection inventive d'une composition appropriée pour le système émulsifiant,

se démarquent très clairement de l'invention selon le WO 93 18 117, que perfectionne la présente invention.

10 Les carburants émulsionnés perfectionnés qui sont dotés de ces caractéristiques, bénéficient d'une grande stabilité au stockage sur de longues périodes de temps. Ils ne déphasent pas (séparation de phase) et ce aussi bien dans des réservoirs que dans les divers éléments constituant les circuits d'alimentation de dispositifs propres à servir de siège à la combustion, à savoir : moteurs à explosion, brûleurs...

L'émulsion selon l'invention reste parfaitement homogène de sorte que les risques d'anomalie de fonctionnement des dispositifs de combustion sont extrêmement limités. Cette absence de déphasage (séparation de phases) et de coalescence, que ce soit par gravité ou par tout autre moyen de séparation (filtration, effet centrifuge...), constitue un progrès technique majeur, qui permet d'envisager concrètement les applications industrielles et commerciales sérieuses.

Il s'agit là de réels perfectionnements par rapport au carburant émulsionné selon le WO 93 18 117.

25 Au sens de la présente invention, la stabilité de l'émulsion s'entend comme un maintien de celle-ci dans son état physicochimique initial d'émulsion homogène (pas de déphasage, pas de coalescence des gouttelettes de phase dispersée), lors d'un stockage d'au moins 3 mois à température ambiante.

Par ailleurs, les combustibles émulsionnés selon l'invention procurent 30 parallèlement des performances tout à fait intéressantes et satisfaisantes, en ce qui concerne la réduction des émissions polluantes et de la consommation, et ce pour un prix de revient raisonnable.

Il est à noter que ces acquis n'ont pas été obtenus au détriment des performances de combustion (rendements thermique et thermomécanique de haut 35 niveau).

De plus, l'absence de gouttelettes de grande taille permet de minimiser les problèmes de colmatage, de perte de charge et/ou de séparation d'eau dans les organes de filtrage, tels que ceux qu'on peut trouver dans des circuits d'alimentation en combustible émulsionné. Ces problèmes se posent, en outre, avec d'autant plus d'acuité par grand froid provoquant le gel des gouttelettes de phase aqueuse, ce qui conduit à la formation de billes ayant une capacité de colmatage supérieure à celle des gouttelettes liquides. L'avatar que cause le gel des gouttelettes peut être minimisé par addition d'antigels.

La valeur moyenne en diamètre de gouttelettes de phase aqueuse fixée à 10 3 µm, de préférence 1 µm et plus préférentiellement encore à 1 µm, et assortie d'un écart-type de 1 µm maximum est apparue comme étant l'un des facteurs déterminant pour garantir la stabilité de l'émulsion et en particulier la limitation des phénomènes de coalescence et de déphasage. Conformément à l'invention, on prévoit donc un profil granulométrique « monodisperse » autour de 1 µm en pratique (Cf courbe de la 15 Figure 5). Cela signifie que la population de gouttelettes est homogène en taille, cette dernière étant en outre suffisamment basse pour concourir à la stabilité.

Au sens de la présente invention, le sigle HLB désigne : "Hydrophile-Lipophile-Balance". Il s'agit d'un paramètre bien connu de caractérisation des émulsifiants. L'ouvrage de référence dans le domaine des émulsions, à savoir : 20 "EMULSIONS : THEORY AND PRACTICE. Paul BECHER - REIN HOLD - Publishing Corp - ACS Monograph - Ed, 1965" donne au chapitre "the chemistry of emulsifying agents" - p. 232 et suivantes - une définition détaillée de l'HLB. Cette dernière est incorporée par référence dans le présent exposé.

25 EXPOSE DETAILLE DE L'INVENTION :

La composition qualitative et quantitative du système émulsifiant est également un élément essentiel de l'invention, qui contribue aux résultats obtenus notamment au regard de la stabilité.

30 Avantagusement, l'émulsion comprend au moins 5 % en poids d'eau et la concentration en système émulsifiant par rapport à la masse totale du combustible est inférieure ou égale à 3 % en poids, de préférence à 2 % en poids.

Conformément à une forme préférée de réalisation de l'invention le système émulsifiant comprend les 3 composés (I), (II) et (III) dans les proportions 35 suivantes :

(I) de 2,5 à 3,5 parties en poids

244

- de préférence 3 parties en poids
 (II) de 1,5 à 2,5 parties en poids
 de préférence 1,5 à 2 parties en poids
 (III) de 0,5 à 1,9 parties en poids
 de préférence 0,5 à 1,5 parties en poids.

5 L'ester d'acide gras et de sorbitan (I) est, de préférence, essentiellement constitué par un ou plusieurs oléates de sorbitan en C_{18} , éventuellement associé à un ou plusieurs esters d'acide gras en C_{18} (linoléique, stéarique) et en C_{16} (palmitique). Naturellement
 10 l'ester (I) n'est pas limité aux monoesters d'acides gras et de sorbitan mais s'étend aux di et/ou au tri-esters et à leurs mélanges. En tout état de cause, l'un des critères de sélection de cet ester (I) est avantageusement l'appartenance à la fourchette d'HLB comprise entre 1 et 9, ce qui lui donne une tendance lipophile marquée. L'HLB plus particulièrement préféré pour l'ester (I) est comprise entre 2,5 et 5,5.

En pratique, on privilégie donc des mélanges d'esters essentiellement
 15 constitués d'oléates et, en quantités plus faibles, de palmitate, stéarate et linoléate de sorbitan. Il peut, par exemple, s'agir ainsi de sesquioléate de sorbitan, du type de ceux commercialisés sous la marque SPAN 83® ou ARLACEL 83® (ICI).

Comme autres exemples d'esters (I) de sorbitan, on peut citer les laurates de sorbitan, du type de ceux commercialisés sous la marque SPAN 20® ou ARLACEL 20® (ICI),
 20 ALKAMULS SML (RHONE POULENC), les stéarates de sorbitan du type de ceux commercialisés sous la marque ARLACEL 60® (ICI) ou ALKAMULS SMS (RHONE POULENC), sans que cette liste soit exhaustive.

Il va de soi que, au sens de la présente invention, les esters (I) s'étendent à tous les analogues et dérivés des esters d'acide gras et sorbitan.

25 S'agissant du composé (II), il est choisi parmi les oléates et/ou les stéarates et/ou les ricinoléates de polyalkyleneglycol et de préférence de polyéthylène glycol (PEG),

de préférence parmi ceux dont le PEG a un poids moléculaire inférieur ou égal à 450, de préférence de l'ordre de 300.

30 Il peut, par exemple, s'agir ainsi de monooléate de PEG 300 du type de ceux commercialisés sous la marque TILOL 163® (UNION DERIVAN SA), EMULSOGEN A® (HOECHST). Comme autres exemples de composés (II), on peut mentionner le monooléate de PEG 400, du type de ceux commercialisés sous la marque SECOSTER MO 400 (STEPAN), REMCOPAL (CECA), ou l'acide
 35 stéarique éthoxylé avec 8 motifs éthoxy (=stéarate de PEG 350) du type de ceux commercialisés sous la marque SIMULSOL M45® (SEPPIC) ou MYRJ 45® (ICI), le

ricinoléate de PEG, du type de ceux commercialisés sous la marque CEREX EL 4929® (AUSCHEM SpA) ou MARLOSOL R70® (HÜLS AG, STEPAN).

L'alcoxylate d'alkylphénol (III) est, de préférence, choisi parmi les nonylphénols et/ou les octylphénols polyéthoxylés, les nonylphénols polyéthoxylés
 5 étant particulièrement préférés.

En pratique, il s'agit e.g. de l'éthoxylate de nonylphénol. Il peut être avantageusement remplacé ou associé par un ou plusieurs autres alcoxylates d'alkylphénol. Il est ainsi intéressant de retenir les alcoxylates d'alkylphénol (III) dans
 10 lesquels le radical alkyle substituant le phénol comporte environ de 1 à 20 atomes de carbone, de préférence de 5 à 20. En outre, il est également préférable de sélectionner les alcoxylates (e.g. éthoxylate) d'alkylphénol dans lesquels la chaîne alcoyle comporte, de préférence de 8 à 20 et, plus préférentiellement encore, de 8 à 15 groupes d'oxyde d'alkylène (e.g. oxyde d'éthylène) par molécule.

En pratique, on privilégie ainsi le nonylphénol polyéthoxylé :

15 $C_9H_{19}-C_6H_4-(OCH_2CH_2)_m-OH$, avec $8 < m < 15$. Il est apparu en effet essentiel dans le cadre de l'invention de recourir à des nonylphénols polyéthoxylés, caractérisés non seulement par leur caractère hydrophile, mais également par des points de trouble, définis au sens de la norme DIN 53917 avec une solution aqueuse à 1% en masse supérieurs à 30° C. Une combinaison de ces caractéristiques a permis en effet
 20 d'obtenir non seulement des systèmes émulsifiants performants pour la préparation d'une émulsion eau-combustible au sens de l'invention, mais, en outre, d'obtenir des propriétés de tenue en température tout à fait remarquables et aptes à rendre cette émulsion stable dans un large domaine de température.

Comme autres exemples de composés (III), on peut citer les octylphénols
 25 polyéthoxylés en particulier ceux commercialisés sous la marque OCTAROX® (SEPPIC) et SINNOPAL OP® (SIDOBRE-SINNOVA).

Suivant une variante préférée de l'invention, le composé (III) du système émulsifiant est un mélange de nonylphénols polyéthoxylés, de préférence de deux nonylphénols polyéthoxylés ayant respectivement 9 et 12 restes oxyde d'éthylène

30 Sans que cela ne soit limitatif, les combustibles plus spécifiquement visés par la présente invention sont ceux dans lesquels l'hydrocarbure ou le mélange d'hydrocarbures entrant dans leur constitution, est (sont) choisi(s) dans le groupe de produits suivants : gazoles, essences, kérosènes, mazouts, carburants de synthèse, huiles végétales estérifiées ou non, et leurs mélanges.

35 De manière plus préférée encore, la présente invention concerne un groupe de combustibles particuliers que sont les carburants (gazoles, essences, kérosènes,

carburants de synthèse, huiles végétales ou animales estérifiées ou non) employés comme combustibles dans des moteurs à explosion ou moteurs thermiques.

Outre les hydrocarbures, l'eau et le système émulsifiant, le combustible ou carburant selon l'invention peut être additionné à l'aide d'un certain nombre de produits ayant diverses fonctionnalités.

Dans ce contexte, l'un des grands intérêts des émulsions *hydrocarbures/eau* selon la présente invention est d'offrir deux types de supports différents pour les additifs, à savoir : un support lipophile constitué par la phase continue hydrocarbure et un support hydrophile constitué par la phase aqueuse. Cela élargit considérablement les possibilités d'introduction de composés additifs actifs. En effet, auparavant, seuls les composés oléosolubles pouvaient être incorporés aisément dans les combustibles et les carburants. Cette contrainte est désormais supprimée grâce à la présente invention, d'autant plus que la solubilité dans l'eau est une propriété offerte à un nombre de produits largement supérieur à celui des produits solubles dans les combustibles au sens de l'invention.

Ainsi, il est envisageable conformément à l'invention, de doter le combustible ou le carburant émulsionné d'une fonction procétane à l'aide d'additifs solubles ou miscible dans l'eau ou bien encore dans les hydrocarbures. Ces additifs peuvent donc être constitués par un ou plusieurs produits procétanes choisis, de préférence, parmi les peroxydes et/ou les nitrates et leurs mélanges. Les nitrates d'alkyle sont des exemples de procétanes susceptibles d'être incorporés dans l'émulsion par l'intermédiaire de la phase hydrocarbures. Les sels de nitrate sont les pendants hydrophiles des nitrates d'alkyles. Leur qualité de sels leur permet d'être supporté par la phase aqueuse.

La fonction anti-suie est une autre fonction qu'il est possible d'apporter dans les combustibles émulsionnés de l'invention. Les promoteurs d'une telle fonction sont avantageusement des additifs constitués par au moins un catalyseur métallique ou alcalinoterreux, aptes à favoriser la réaction de post-combustion des suies, ledit catalyseur étant de préférence à base de magnésium, calcium, barium, cérium, cuivre, fer ou leurs mélanges. Ces promoteurs catalytiques de destruction des suies sont d'autant plus faciles à introduire que ce sont généralement des composés dont les sels sont solubles dans l'eau, ce qui les rend compatibles avec la phase aqueuse des émulsions selon l'invention. Il n'en va pas de même pour les combustibles classiques de l'art antérieur exclusivement constitués d'hydrocarbures hydrophobes.

Selon une variante de l'invention, il peut être avantageux de conférer des propriétés biocides, voire bactéricides aux combustibles émulsionnés. Ceux-ci peuvent donc éventuellement comprendre au moins un biocide, de préférence un bactéricide.

La fonction détergente peut également s'avérer intéressante pour les émulsions selon l'invention. Il convient donc d'envisager le cas où ces dernières comprennent un ou plusieurs agents ou additifs détergents.

La fonction antioxyde d'azote (NO_x) qui peut être apportée par des composés ammoniacés (du type urée, ammoniac), est également prise dans les combustibles et plus particulièrement dans les carburants.

On peut également rajouter une fonction anti-gel ou combustible émulsionné, en lui rajoutant des additifs anti-gels tels que des glycols ou des solutions salines.

Pour fixer les idées, un exemple pratique de composition de combustible émulsionné selon l'invention est donné ci-après :

15	- hydrocarbure(s)	50 à 99 % de préférence 65 à 99 %
	- eau	0,1 à 50 % de préférence 1 à 35 %
	- système émulsifiant	0,05 à 5 % de préférence 0,1 à 3 %
	- additifs	0,01 à 5 % de préférence 0,05 à 2 %

Par ailleurs, la présente invention est parfaitement en phase avec le courant actuel d'utilisation de "pétrole vert" à titre de substituant partiel de carburant, notamment diesel. On peut ainsi envisager avantageusement l'incorporation d'au moins une huile végétale ou animale estérifiée ou non et/ou d'au moins un extrait de celle-ci, de préférence à raison de 1 à 60 % en poids.

Il peut s'agir par exemple d'huiles de colza, de soja ou de tournesol estérifiées ou non, qui peuvent entrer dans la composition de carburant à hauteur de 5 %, 30 % ou bien encore 50 % en masse par exemple.

La présente invention concerne également une composition d'additifs pour carburant comprenant essentiellement :

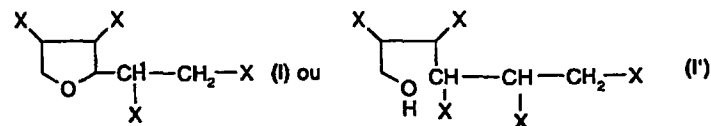
- le système émulsifiant décrit supra
- et éventuellement au moins un autre additif, de préférence choisi parmi les produits décrits ci-dessous, à savoir : procétanes, promoteurs catalytiques de combustion des suies, biocides, détergents, composés ammoniacés, anti-gels, huiles végétales estérifiées ou non et leurs mélanges.

Selon un autre de ces aspects, la présente invention concerne un procédé d'obtention d'un combustible émulsionné caractérisé en ce qu'il consiste essentiellement de manière simultanée ou non :

246

- a - à mettre en oeuvre au moins un hydrocarbure, de l'eau et un système émulsifiant comprenant :

Δ (I) au moins un ester de sorbitol de formule générale :

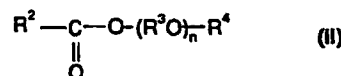


dans laquelle :

- les radicaux X sont identiques ou différents entre eux et correspondent chacun à : OH, R¹COO- avec R¹ représentant un radical hydrocarboné aliphatique, saturé ou insaturé, linéaire ou ramifié, éventuellement substitué par des hydroxyles et ayant de 7 à 22 atomes de carbone, R¹ étant de préférence un reste acide gras privé d'un carboxyle terminal,

cet ester (I) présentant une HLB comprise ou égale à 1 et 9 ;

Δ (II) au moins un ester d'acide gras de formule générale :



dans laquelle :

- R² représente un radical hydrocarboné aliphatique, saturé ou insaturé, linéaire ou ramifié, éventuellement substitué par des fonctions hydroxyles et ayant de 7 à 22 atomes de carbone, R² étant de préférence un reste acide gras privé d'un carboxyle terminal,
- R³ étant un alkylène linéaire ou ramifié en C₁-C₁₀, de préférence en C₂-C₃,
- n est un nombre entier supérieur ou égal à 6 de préférence compris entre 6 et 30,
- R⁴ correspond à : H, alkyle linéaire ou ramifié en C₁-C₁₀,

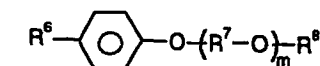


24A

avec R⁵ répondant à la même définition que celle donnée supra pour R² ;

cet ester (II) ayant de préférence une HLB supérieure ou égale à 9 ;

Δ (III) et/ou au moins un alkylphénolpolyalcoxyolé de formule générale :



dans laquelle :

- R⁶ représente un alkyle linéaire ou ramifié en C₁-C₂₀, de préférence en C₅-C₂₀ ;
 - m est un nombre entier supérieur ou égal à 8, de préférence compris entre 8 et 15,
 - R⁷ et R⁸ répondent respectivement aux mêmes définitions que celles données supra pour R³ et R⁴ de la formule (II),
- cet ester (III) ayant de préférence une HLB comprise entre 10 et 15 ;
- ce système émulsifiant ayant une HLB comprise entre 6 et 8 de préférence entre 6,5 et 7,5.

▷ et d'éventuels autres additifs ;

- b - à mélanger ces constituants de manière à former une émulsion eau dans huile,
- c - et à soumettre l'émulsion à un fractionnement de manière à réduire la taille des gouttelettes de phase dispersée aqueuse à une taille moyenne inférieure ou égale à 3 µm, de préférence 2 µm et plus préférentiellement encore 1 µm, avec un écart-type inférieur à 1 µm.

Le procédé selon l'invention peut donc être résumé à une formation d'émulsion et un fractionnement de cette émulsion, de manière à réduire la taille des gouttelettes de phase dispersée aqueuse jusqu'à obtenir et maintenir une granulométrie monodisperse de 1 µm avec un écart type inférieur à 1 µm.

La mise en émulsion repose en grande partie sur le système émulsifiant. Ce dernier a de préférence la composition suivante :

- (I) de 2,5 à 3,5 parties en poids
- de préférence 3 parties en poids

24A

(II) de 1,5 à 2,5 parties en poids
de préférence 1,5 à 2 parties en poids

(III) de 0,5 à 1,9 parties en poids
de préférence 0,5 à 1,5 parties en poids.

5 Le procédé selon l'invention peut être l'un de ceux utilisables pour préparer le combustible (e.g. carburant) émulsionné perfectionné décrit supra. Il s'ensuit que par extension, les caractéristiques et les observations données dans la description ci-dessus à propos des produits mis en oeuvre dans l'émulsion, peuvent être intégralement transposées dans cette partie de l'exposé relatif au procédé.

10 Le fractionnement de l'émulsion est un traitement mécanique ou thermomécanique visant à rompre la force de cohésion des gouttelettes, de manière à promouvoir leur subdivision. Les moyens de fractionnement préférentiellement mis en oeuvre lors de l'étape (c), sont du type mélangeur statique, pompe centrifuge ou autre, broyeur colloïdal ou autre, mélangeur à rotor, mélangeur à ultra-son et autre procédé de fragmentation d'un liquide dans un autre liquide non miscible.

15 En pratique, on peut utiliser les mélangeurs statiques à titre de moyens de fractionnement. Ces mélangeurs statiques sont des organes au travers desquels on fait passer l'émulsion à grande vitesse et dans lesquels celle-ci subit de brusques changements de direction et/ou de diamètre des canalisations qui composent l'intérieur des mélangeurs. Ce qui conduit à une perte de charge, qui est un facteur d'obtention d'une émulsion correcte en finesse et stabilité.

20 Comme autres exemples de procédé de fabrication d'une émulsion, et suivant l'échelle de production visée, on peut utiliser un mélangeur à rotor du type de ceux commercialisés sous la marque ULTRA-TURRAX®, un homogénéisateur haute pression du type de ceux commercialisés par APV-BAKER ou tout procédé connu de l'homme de l'art et permettant une extrapolation d'échelle aisée.

25 Selon une variante de mise en oeuvre du procédé de l'invention, les étapes b et c de mélange/fractionnement sont, par exemple, séquentielles, c'est-à-dire que la procédure consiste à mélanger dans un premier temps l'(ou les) hydrocarbure(s) et le système émulsifiant et les éventuels additifs, le prémélange étant dans un deuxième temps mélangé et émulsionné avec l'eau.

30 Selon une autre variante du procédé de l'invention, on prévoit une mise en oeuvre des étapes - a - à - c - selon un mode continu.

35 Les étapes - a - à - c - du procédé selon l'invention se déroulent à température ambiante, qui est aussi celle des fluides et des matières premières mises en oeuvre.

APPLICATION INDUSTRIELLE :

5 Compte-tenu de ces avantages en termes de stabilité, de faible pouvoir polluant, de faible consommation et de prix, le combustible émulsionné conforme à l'invention et/ou obtenu par le procédé selon l'invention, est voué à de multiples applications industrielles et commerciales.

10 Le secteur visé en premier chef, mais toutefois non exclusivement, est celui des carburants, en particulier le gazole. Il devrait donc être possible désormais de proposer au propriétaire de véhicules ou autres engins à moteur thermique (e.g. diesel) des carburants émulsionnés comprenant de 5 à 15 % en poids d'eau, sans qu'il soit nécessaire de modifier les réglages des moteurs.

15 En outre, moyennant quelques adaptations relativement mineures des moteurs, ceux-ci pourront fonctionner efficacement, économiquement et de manière peu polluante, avec des carburants émulsionnés comprenant de 35 à 45 % en poids d'eau.

20 Cela représente un progrès technique considérable dans le domaine des carburants. Il est également possible d'escompter des retombées bénéfiques dans le domaine des combustibles pour machines thermiques telles que des chaudières, des fours, des turbines à gaz, des générateurs etc. Dans de tels cas, le combustible concerne peut être le mazout.

25 La présente invention sera mieux comprise à la lumière des exemples qui suivent et qui décrivent la préparation, la caractérisation structurelle et fonctionnelle des carburants émulsionnés selon l'invention, de même que des tests comparatifs montrant la supériorité des émulsions selon l'invention par rapport à l'art antérieur le plus proche. Ces exemples mettent également en exergue tous les avantages et les variantes de mise en oeuvre de ces émulsions *hydrocarbures/eau*.

L'illustration des exemples est réalisée à l'aide des figures 1 à 4 annexées.

DESCRIPTION DES FIGURES

30 La figure 1 représente une photographie au microscope optique avec un grossissement donné d'une émulsion *eau/gazole* conforme à l'invention, avec des gouttelettes de phase dispersée aqueuse, de taille inférieure ou égale à 1 µm.

35 La figure 2 représente une photographie au microscope optique avec le même grossissement que celui de la figure 1 d'une émulsion *eau/gazole* conforme à l'art antérieur le plus proche, avec des gouttelettes de phase dispersée aqueuse, de taille supérieure ou égale à 10 µm.

La figure 3 représente un schéma d'un exemple de dispositif de fractionnement d'émulsion, susceptible d'être mis en oeuvre dans le procédé selon l'invention.

La figure 4 représente un graphe d'un régime moteur (tour/minute) cyclique en fonction du temps t (seconde), imposé à des bus équipés d'un moteur diesel, pour la réalisation de tests de caractérisation fonctionnelle des carburants émulsionnés selon l'invention et selon l'art antérieur. (Exemple II).

La figure 5 représente un graphe de la répartition granulométrique monodisperse d'un carburant émulsionné suivant l'invention, dans lequel est reporté en abscisse le diamètre moyen $\bar{d}$ des gouttelettes de la phase aqueuse et en ordonnée $\Delta N/N$, N étant le nombre total des gouttelettes et ΔN le nombre de gouttelettes d'un $\bar{d}$ donné.

La figure 6 représente les cycles de variations de température et d'agitation appliqués aux formulations été (fig. 6.1) et hiver (fig. 6.2) pour déterminer leur stabilité en utilisation.

EXEMPLES

EXEMPLE I :

On a préparé, selon la méthode intégrant les étapes a), b) et c) citée ci-dessus, plusieurs émulsions avec différentes compositions du système émulsifiant. Pour les besoins de la comparaison, la quantité totale d'agents tensioactifs a été maintenue constante et égale à 1,86 % en poids par rapport au poids total de l'émulsion. La quantité totale de solution aqueuse (eau + éventuels additifs hydrosolubles tel que les biocides ou un antigel) est constante et égale à 13 % en poids dans toutes les formulations.

La formulation standard est détaillée dans le tableau 1.

Tableau 1 : Formulation utilisée pour les exemples comparatifs

Composé	Référence (fournisseur)	composition (% poids)
Procétane	RV 100 (ELF ANTAR FRANCE)	0,87
Système émulsifiant	selon les exemples	1,86
Eau	selon les exemples	13*
Gazole	CEC RF 0387	84,27
Biocide Gazole	EB 7301 (ELF ANTAR FRANCE)	A**
Biocide Eau	EB 301 W (ELF ANTAR FRANCE)	B***

* L'eau dans la formulation hiver est additivée par 10 % poids de MEG (monoéthylèneglycol).

** A : dose de 1 pour 1000, par rapport au volume de gazole

*** B : dose de 2 pour 1000, par rapport au volume d'eau.

Les compositions des systèmes émulsifiants testés sont données dans le tableau 2. Dans ce tableau 2, les compositions ont été présentées sous forme des proportions pondérales de chacun des constituants du système émulsifiant, étant précisé que celui-ci représente 1,86 % en poids de la formulation d'émulsion finale.

Pour l'interprétation du tableau 2, on peut préciser que

- les compositions A à F sont celles de l'invention,
- la composition G est celle décrite dans WO-93/18117.
- les compositions H à L servent d'exemples comparatifs démontrant la supériorité des compositions de l'invention sur celles ne comportant que deux des constituants ou celles présentant une HLB sortant de la gamme revendiquée.

Tableau 2 :

Composition	A	B	C	D	E	F	G	H	I	J	K	L
Tensioactif												
Sesquioléate de sorbitan	3	3		1,5	1,5	1,5	1				1,5	1
Monooléate de sorbitan			3			1,5		1,5	1,5	1,5		
Laurate de sorbitan				1							1,5	
Stéarate de sorbitan					1,5							
PEG 300							1					
Monooléate de PEG 300	2		2	2	2	1					2	2
Monooléate de PEG 600								1				
Ricinoléate de PEG 300		2				1						
Nonylphénol éthoxylé 9 E0	1	1,5	1	1	1	1,5	1					3
Nonylphénol éthoxylé 12 E0	0,5		0,5						1			
Nonylphénol éthoxylé 30 E0										1	1,5	
Octylphénol-éthoxylé 9 E0					0,5							
HLB du système émulsifiant	7,5	7,7	7,6	6,5	7,8	7,9	8,2	10,1	8,1	9,2	9,6	10,1

La qualité de l'émulsion obtenue est caractérisée par les critères ci-après.

5 Critère granulométrique

Il s'établit par l'aspect homogène des gouttelettes d'eau dispersées dans la phase continue gazole, avec une faible polydispersité, une taille moyenne des particules

inférieure à 1 μm , avec un écart-type inférieur à 1 μm , établi par analyse d'images à partir de microphotographies.

Critère de stabilité

- 5 Ce critère est double et vise la stabilité dans des conditions d'utilisation (caractère dynamique) ainsi que la stabilité au stockage à différentes températures.

La stabilité en utilisation

- 10 Elle est caractérisée par une absence de démixtion/décantation ou autre rupture de l'émulsion observée sur un échantillon de 1 litre placé dans un récipient de verre à fond plat (type bécher), ayant subi un cycle simulant l'évolution de température du carburant séjournant dans un réservoir. On dit qu'il y a démixtion quand le volume du surnageant, correspondant à un relargage du gazole, est supérieur à 5 % du volume total de l'échantillon, ou quand il y a apparition d'un pied d'eau au fond du bécher.

- 15 Pour chaque formulation « été » et « hiver », le profil du cycle de variation des températures est illustré Figure 6. On notera que le système doit être agité (agitation mécanique douce, environ 60 t/mn), ou au repos selon la phase du cycle. La Figure 6.1. illustre le cycle formulation été et la Figure 6.2. celui de la formulation hiver.

20

La stabilité au stockage

Elle est caractérisée par une absence de démixtion/décantation après 3 mois de stockage statique dans des fioles tronconiques, pour 3 échantillons placés respectivement à 0°C, 20°C, et 40°C.

- 25 Ces critères ont été appliqués aux formulations obtenues à partir des compositions A à L, telles que décrites dans le tableau 3. Les résultats sont fournis dans le tableau 3. Certaines formulations sont additivées également par du méthanol (MeOH) en solution dans l'eau, le pourcentage étant exprimé en volume par rapport au volume de la formulation totale ou par de l'ester méthylique de colza (EMC) en solution dans le gazole, le pourcentage étant exprimé en volume par rapport à celui de la formulation totale.
- 30

Formulation	416	silver	416	416	416	416	416	416	416	416	416	416	416	416	416
Adhésif spécifique	-	-	9% BAC	-	-	-	-	-	-	7%	7%	7%	7%	-	-
Dispositif de soudure (d)	non	non	non	non	non	non	non	non	non	poly	poly	poly	poly	poly	poly
Substrat en utilisation	cu	cu	cu	cu	cu	cu	cu	cu	cu	1-10 µm	1-30 µm	1-30 µm	1-30 µm	1-30 µm	1-30 µm
stabilité stockage	an														
Δ 0°C	4 s	3 m	3 s	4 s	3,5 s	4 s	4 s	4 s	4 s	th	th	th	th	th	th
Δ 10°C	3 m	3 m	3 m	3 m	6 s	3 m	3 m	3 m	3 m	1 j	1 j	1 j	1 j	2 h	2 h
Δ 40°C	3 m	4 s	3 m	3 m	4 s	3 m	3 m	3 m	3 m	1 j	1 h	1 h	1 h	1 h	1 h

Dans le tableau 3, les abréviations suivantes ont été utilisées :

h = heure

j = jour

s = semaine

m = mois

5

La stabilité au stockage s'apprécie par le temps plus ou moins long pour que la formulation présente le phénomène de démixtion.

EXEMPLE II : PREPARATION D'UNE EMULSION GAZOLE/EAU/SYSTEME EMULSIFIANT (SELON L'INVENTION ET SELON L'ART ANTERIEUR LE PLUS PROCHE)

10 II.1. EMULSION SELON L'INVENTION (EMULSION 3 : 2 : 1)

ETAPE - 2 -

II.1.1. - Pour la préparation de 200 kg d'émulsion, les matériaux de départ mis en oeuvre sont les suivants :

- 15 - 164 kg de gazole,
- 4 kg de système émulsifiant (SE) ;
- 2 kg d'un procétane du type nitrate d'alkyle commercialisé sous la
référence CI 0801 par la Société OCTEL,
- 30 kg d'eau du réseau.

II.1.2. Obtention du système émulsifiant :

20 Les 4 kg de système émulsifiant sont obtenus en mélangeant dans un mélangeur à hélices tournant à quelques centaines de tours/min pendant quelques minutes :

- 25
- 3 parties en poids, soit 2 kg de SORBITHOM® S06 commercialisé par la société UNION DERIVAN SA,
 - 2 parties en poids, soit 1,333 kg de monoooléate de polyéthylène glycol de marque TILOL® 163 commercialisé par la société UNION DERIVAN SA ;
 - 1 partie en poids, soit 0,666 kg d'éthoxylate de nonylphénol du type de celui commercialisé sous la marque NONILFENOL® 9M OXIETHIL® par la Société UNION DERIVAN SA.

30 Ce système émulsifiant présente une HLB de 7,2.

ETAPES - b - ET - c - PREMELANGE - FORMATION - EMULSION ET FRACTIONNEMENT

On incorpore les 4 kg de système émulsifiant dans les 164 kg de gazole et l'on homogénéise ce mélange à l'aide de l'agitateur à hélice tournant à un régime de quelques centaines de tours/min pendant quelques minutes. Au cours de l'agitation, on

ajoute les 2 kg de procétane, les 30 kg d'eau étant ajoutés juste avant le fractionnement décrit ci-après.

Le dispositif mis en oeuvre est celui représenté à la figure 3. Ce dispositif est constitué :

- 5 - par un récipient 1 destiné à contenir un liquide 2 formé par tous les constituants de l'émulsion à l'exclusion de l'eau avant fractionnement ou par l'émulsion stabilisée en fin de fractionnement ;
- par des moyens de fractionnement 3 stricto sensu,
- et par un circuit 4 d'alimentation en eau (E).

- 10 Le récipient 1 est un conteneur classique, qui est alimenté de manière continue ou discontinue en prémélange *gazole/système émulsifiant/additif*.

- Les moyens de fractionnement 3 comprennent un mélangeur statique 5 du type de ceux de type SMV - 4DM 20 (5 éléments de mélange en série) commercialisés par la Société SULZER. Ce mélangeur est constitué par un cylindre creux présentant une
- 15 entrée et une sortie de fluide et définissant, à l'intérieur du cylindre, un parcours en zig-zag pour le fluide, à l'aide de plusieurs étages de cloisons transversales pourvue de fentes obliques formant des canalisations de passage de fluide. La sortie du mélangeur statique 5 est relié à un conduit 6 débouchant à l'intérieur du récipient 1 (moyens d'acheminement 6 de l'effluent dans le récipient 1), tandis que son entrée est connectée
- 20 à un conduit 7 équipé d'une pompe 8. L'extrémité libre 9 de cette canalisation 7 plonge dans le bain de prémélange ou d'émulsion 2 contenu dans le récipient 1. Elle est par ailleurs reliée en amont et au voisinage de l'entrée de pompe 8 à une canalisation 10 d'alimentation en eau, qui forme avec la vanne 11, le circuit 4 évoqué ci-dessus. Ce dispositif est de nature à assurer une importante perte de charge, à débit
- 25 nominal, de manière à provoquer la dispersion de l'émulsion.

Le fractionnement à l'aide de ce dispositif s'opère de la manière suivante : après remplissage du récipient 1 par le prémélange *gazole/SE/additifs*, la pompe 8 est mise en fonctionnement de manière à instaurer une circulation de fluide au travers du mélangeur statique 5. On ouvre alors l'électrovanne 11 pour assurer l'alimentation en

- 30 eau et le mélange de celle-ci avec le prémélange *G/SE/A* au sein de la pompe 8, ce mélange étant ensuite acheminé vers le mélangeur statique pour y subir le fractionnement souhaité. La pression du fluide en sortie de pompe 8 est de 5 MPa.
- Dans le présent exemple, les 30 kg d'eau sont introduits en environ 1 min. Le système fonctionne en boucle pour assurer un fractionnement pendant 30 min. On
- 35 obtient ainsi 200 kg d'émulsion répondant aux caractéristiques de l'invention. Cette

émulsion présente une couleur blanchâtre et une viscosité cinématique de 6,2 mm²/s à 20°C.

II.2. EMULSION SELON LES PROPORTIONS DE L'ART ANTERIEUR (EMULSION 1 : 1 : 1)

- On prépare également 200 kg d'émulsion avec 164 kg de gazole, 4 kg de
- 5 système émulsifiant, 2 kg d'additifs constitué par de l'oxyde de magnésium et du toluène et 30 kg d'eau.

Les proportions de SORBITHOM® S06 : TILOL 163® : NONILFENOL® 9 M OXIETHIL® sont de 1 : 1 : 1 et non de 3 : 2 : 1 comme prévu au paragraphe II.1. ci-dessus. Ce système émulsifiant présente une HLB de 8,7.

- 10 Le protocole opératoire mis en oeuvre est celui décrit dans la demande de brevet PCT WO 93/18 117.

LES 200 KG D'EMULSION OBTENUS AINSI SONT DE COULEUR BLANCHATRE.

EXEMPLE III : CARACTERISATION STRUCTURELLE ET FONCTIONNELLE DES EMULSIONS I.1. ET I.2. DE L'EXEMPLE I

- 15 A - STABILITE

1 - Observations au microscope

- Les figures 1 et 2 annexées montrent clairement la différence de profil dimensionnel des gouttelettes de phase dispersée aqueuse. Dans le cas de l'émulsion
- 20 II.1., on peut constater une homogénéité de diamètre des gouttelettes, avec une valeur maximale de l'ordre du µm ce qui établit la monodispersion des gouttelettes. Contrairement à cela, les gouttelettes d'eau de l'émulsion II.2. connues montrent une très grande disparité dimensionnelle, avec une majorité de gouttelettes de taille supérieure à 5 µm et une proportion non négligeable de gouttelettes de taille supérieure à 10 µm.

- 25 2 - Essais de stabilité lors d'un usage réel sur bus de transport en commun

Les bus utilisés pour ces essais sont des véhicules Renault Véhicules Industriels® de type R312, présentant un réservoir de gazole doté d'un soutirage en point bas, de façon à éviter le désamorçage de la pompe à injection en cas de freinage, de virage, ou de côte.

- 30 On approvisionne un premier bus avec 300 litres de l'émulsion selon II.1. et un deuxième bus comparatif également avec 300 litres de l'émulsion selon II.2. Les deux bus effectuent un parcours de 100 km urbain. Ils sont ensuite mis à l'arrêt pendant 48 heures.

23 JAN 1964

On mesure les tensions exercées en solution dans ces conditions d'équilibre. Les données sont les suivantes :

à 25°C : $E_{\text{cell}} = 0,100 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 30°C : $E_{\text{cell}} = 0,105 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 35°C : $E_{\text{cell}} = 0,110 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 40°C : $E_{\text{cell}} = 0,115 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 45°C : $E_{\text{cell}} = 0,120 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 50°C : $E_{\text{cell}} = 0,125 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 55°C : $E_{\text{cell}} = 0,130 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 60°C : $E_{\text{cell}} = 0,135 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 65°C : $E_{\text{cell}} = 0,140 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 70°C : $E_{\text{cell}} = 0,145 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 75°C : $E_{\text{cell}} = 0,150 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 80°C : $E_{\text{cell}} = 0,155 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 85°C : $E_{\text{cell}} = 0,160 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 90°C : $E_{\text{cell}} = 0,165 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 95°C : $E_{\text{cell}} = 0,170 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})
à 100°C : $E_{\text{cell}} = 0,175 \text{ V}$ (pour une solution de Fe^{2+} - Fe^{3+})

[illegible]

EXERCISE IV : INITIATION ET CANCELLATION D'UNE EMISION

[illegible]

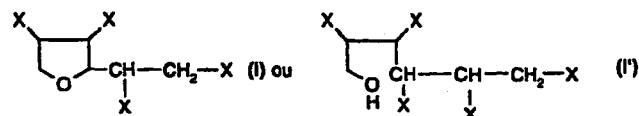
REVENDICATIONS :

1 - Combustible perfectionné, comprenant une émulsion d'eau dans au moins un hydrocarbure, caractérisé

→ en ce que cette émulsion comporte un système émulsifiant

5 comprenant :

Δ (I) au moins un ester de sorbitol de formule générale :

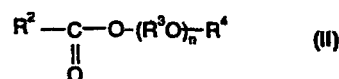


dans laquelle :

- les radicaux X sont identiques ou différents entre eux et correspondent chacun à : OH, R¹COO- avec R¹ représentant un radical hydrocarboné aliphatique, saturé ou insaturé, linéaire ou ramifié, éventuellement substitué par des hydroxyles et ayant de 7 à 22 atomes de carbone, R¹ étant de préférence un reste acide gras privé d'un carboxyle terminal,

cet ester (I) présentant une HLB comprise entre 1 et 9 ;

Δ (II) au moins un ester d'acide gras de formule générale :



dans laquelle :

- R¹ représente un radical hydrocarboné aliphatique, saturé ou insaturé, linéaire ou ramifié, éventuellement substitué par des fonctions hydroxyles et ayant de 7 à 22 atomes de carbone, R¹ étant de préférence un reste acide gras privé d'un carboxyle terminal,
- R³ étant un alkylène linéaire ou ramifié en C₁-C₁₀, de préférence en C₂-C₃,
- n est un nombre entier supérieur ou égal à 6 de préférence compris entre 6 et 30,

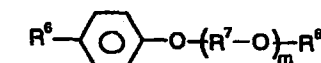
- R⁴ correspond à : H, alkyle linéaire ou ramifié en C₁-C₁₀,



avec R⁵ répondant à la même définition que celle donnée supra pour R² ;

cet ester (II) ayant de préférence une HLB supérieure ou égale à 9 ;

Δ (III) au moins un alkylphénolpolyalcoylé de formule générale :



dans laquelle :

- R⁶ représente un alkyle linéaire ou ramifié en C₁-C₂₀, de préférence en C₃-C₂₀ ;
- m est un nombre entier supérieur ou égal à 8, de préférence compris entre 8 et 15,
- R⁷ et R⁸ répondent respectivement aux mêmes définitions que celles données supra pour R³ et R⁴ de la formule (II),
- cet ester (III) ayant de préférence une HLB comprise entre 10 et 15 ;

→ en ce que ce système émulsifiant a une HLB globale comprise entre 6 et 8, de préférence entre 6,5 et 7,5.

→ et en ce que l'émulsion est réalisée de telle sorte que la taille moyenne des gouttelettes de phase dispersée aqueuse soit inférieure ou égale à 3 μm, de préférence à 2 μm et plus préférentiellement encore à 1 μm, avec un écart-type inférieur à 1 μm.

2 - Combustible selon la revendication 1, caractérisé en ce que l'émulsion comprend au moins 5 % en poids d'eau et en ce que la concentration en système émulsifiant par rapport à la masse totale du combustible est inférieure ou égale à 3 % en poids, de préférence à 2 % en poids.

3 - Combustible selon la revendication 1 ou la revendication 2, caractérisé en ce que le système émulsifiant comprend les composés (I), (II) et (III) et en ce que les proportions en ces composés sont les suivantes :

- (I) de 2,5 à 3,5 parties en poids de préférence 3 parties en poids
- (II) de 1,5 à 2,5 parties en poids

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dans laquelle :

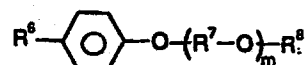
- R² représente un radical hydrocarboné aliphatique, saturé ou insaturé, linéaire ou ramifié, éventuellement substitué par des fonctions hydroxyles et ayant de 7 à 22 atomes de carbone, R² étant de préférence un reste acide gras privé d'un carboxyle terminal,
- R³ étant un alkylène linéaire ou ramifié en C₁-C₁₀, de préférence en C₂-C₃,
- n est un nombre entier supérieur ou égal à 6 de préférence compris entre 6 et 30,
- R⁴ correspond à : H, alkyle linéaire ou ramifié en C₁-C₁₀,



avec R³ répondant à la même définition que celle donnée supra pour R² ;

cet ester (II) ayant de préférence une HLB supérieure ou égale à 9 ;

Δ (III) au moins un alkylphénolpolyalcoylé de formule générale :



dans laquelle :

- R⁶ représente un alkyle linéaire ou ramifié en C₁-C₂₀, de préférence en C₃-C₂₀ ;
 - m est un nombre entier supérieur ou égal à 8, de préférence compris entre 8 et 15,
 - R⁷ et R⁸ répondent respectivement aux mêmes définitions que celles données supra pour R³ et R⁴ de la formule (II),
- cet ester (III) ayant de préférence une HLB comprise entre 10 et 15 ;

Ce système émulsifiant ayant une HLB comprise entre 6 et 8 de préférence entre 6,5 et 7,5.

▷ et d'éventuels autres additifs ;

- b - à mélanger ces constituants de manière à former une émulsion eau dans huile,

- c - et à soumettre l'émulsion à un fractionnement de manière à réduire la taille des gouttelettes de phase dispersée aqueuse à une taille moyenne inférieure ou égale à 3 μm, de préférence 2 μm et plus préférentiellement encore 1 μm, avec un écart-type inférieur à 1 μm.

13 - Procédé selon la revendication 12, caractérisé en ce que le système émulsifiant employé a la composition suivante :

- (I) de 2,5 à 3,5 parties en poids de préférence 3 parties en poids
- (II) de 1,5 à 2,5 parties en poids de préférence 1,5 à 2 parties en poids
- (III) de 0,5 à 1,9 parties en poids de préférence 0,5 à 1,5 parties en poids.

14 - Procédé selon la revendication 12 ou 13 caractérisé en ce que lors de l'étape - c -, l'on met en oeuvre des moyens de fractionnement du type tamis, mélangeur statique, mélangeur à rotor, mélangeur à ultra-sons.

15 - Dispositif pour la mise en oeuvre du procédé selon l'une quelconque des revendications 10 à 14, caractérisé en ce qu'il comprend essentiellement :

- au moins un récipient (1) susceptible de contenir un prémélange (2) hydrocarbure(s)/système émulsifiant/additif(s) et/ou l'émulsion comprenant tout ou partie de l'eau qui rentre dans sa constitution,
- des moyens (3) de fractionnement de l'émulsion comportant, de préférence, au moins un mélangeur statique (5) dont l'entrée est reliée à un conduit (7) pourvu d'au moins une pompe (8) et dont l'extrémité libre (9) est destinée à plonger dans le conteneur (2) du récipient (1), la sortie du mélangeur (5) étant connectée à des moyens d'acheminement (6) de l'effluent dans le récipient (1),
- et d'un circuit (4) d'alimentation en eau, de préférence comprenant au moins une canalisation (10) équipée d'une vanne (11) et reliée au conduit (7) en amont de la pompe (8).

252

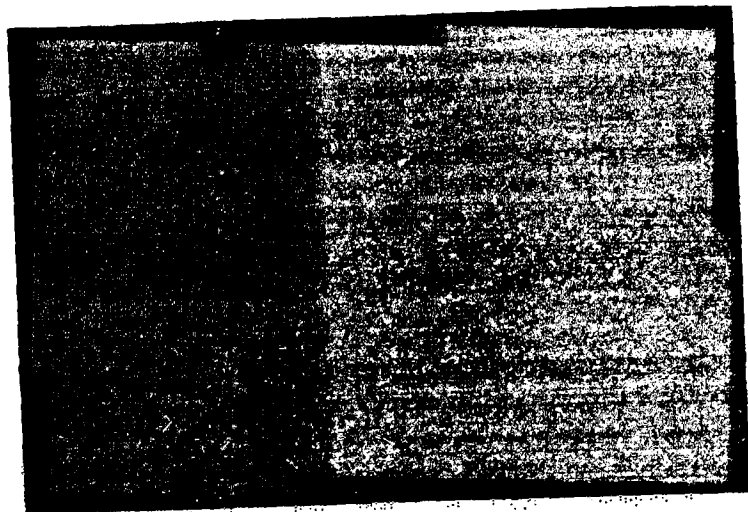


FIG_1

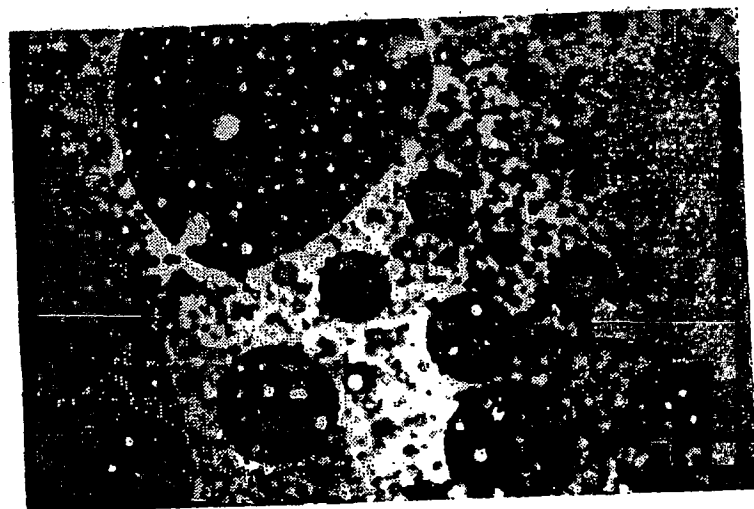


FIG_2

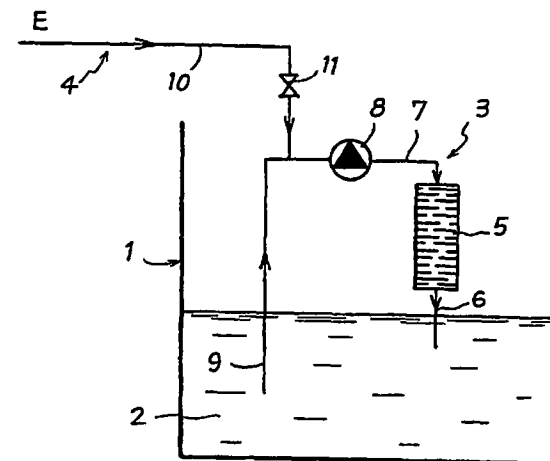


FIG_3

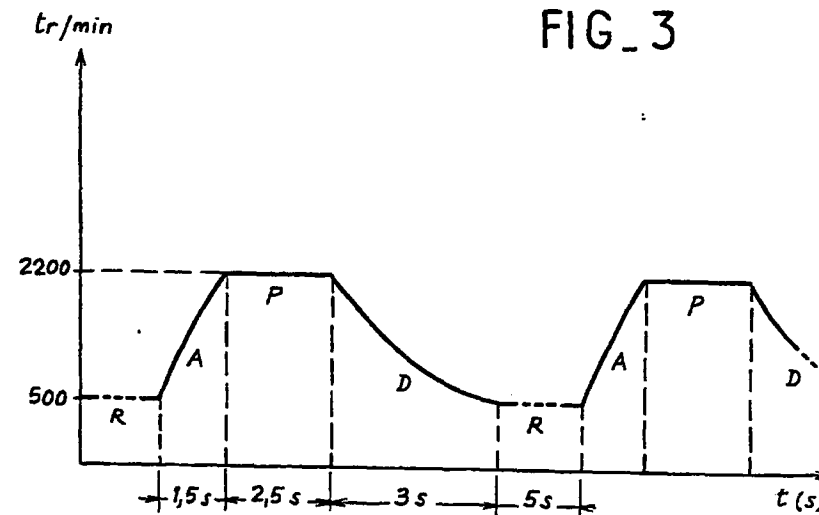


FIG_4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/FR 97/00475

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9318117 A	16-09-93	FR 2688225 A DE 69310981 D EP 0630398 A	10-09-93 26-06-97 28-12-94
GB 2217229 A	25-10-89	NONE	
CH 678283 A	30-08-91	NONE	

RAPPORT DE RECHERCHE INTERNATIONALE

Demande Internationale No
PCT/FR 97/00475

A. CLASSEMENT DE L'OBJET DE LA DEMANDE CIB 6 C10L1/32		
Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB		
B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE Documentation mutuelle consultée (système de classification suivi des symboles de classement) CIB 6 C10L		
Documentation consultée autre que la documentation mutuelle dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche		
Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si cela est réalisable, termes de recherche utilisés)		
C. DOCUMENTS CONSIDERES COMME PERTINENTS		
Catégorie	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
A	WO 93 18117 A (ECOTEC) 16 Septembre 1993 cité dans la demande voir revendications 1-10,51 voir page 8, ligne 8 - ligne 24	1-6,8,9
A	GB 2 217 229 A (ENERSOLVE CHEMICAL COMPANY LIM ;UNIV CITY (GB)) 25 Octobre 1989 voir revendications 1,6,7,10,11	1,10
A	CH 678 283 A (ZUGOL) 30 Août 1991 voir revendications 1,4	1
☐ Voir la liste du cadre C pour la fin de la liste des documents ☒ Les documents de familles de brevets sont indiqués en annexe		
* Catégories spéciales de documents cités: "A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent "E" document antérieur, mais publié à la date de dépôt international ou après cette date "L" document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre invention ou pour une raison spéciale (elle qu'indiquée) "O" document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens "P" document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée "T" document ultérieur publié après la date de dépôt international ou la date de priorité et n'appartenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention "X" document particulièrement pertinent l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive par rapport au document considéré (soitement) "Y" document particulièrement pertinent l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est antérieur à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier "Z" document qui fait partie de la même famille de brevets		
Date à laquelle la recherche internationale a été effectivement achevée 30 Juin 1997		Date d'expiration du présent rapport de recherche internationale 08.07.97
Nom et adresse postale de l'administration chargée de la recherche internationale Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL - 2220 HV Rijswijk Tél. (+ 31-70) 340-2040, Tr. 31 631 epo nl. Fax (+ 31-70) 340-3016		Fonctionnaire autorisé De Herdt, O

DEMANDE DE BREVET EUROPEEN

Numéro de dépôt: 85400499.1

Int. Cl.: C 07 C 77/02, C 07 C 76/04,
C 10 L 1/22

Date de dépôt: 14.03.85

Projeté: 20.03.84 FR 8404423

Demandeur: INSTITUT FRANCAIS DU PETROLE, 4,
Avenue de Bois-Préau, F-92502 Neuilly-Malmaison (FR)

Date de publication de la demande: 09.10.85
Bulletin 85/41

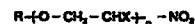
Inventeur: Born, Maurice, 72, rue du Vieux Pont,
F-92000 Nanterre (FR)
Inventeur: Guilbet, Jean-Claude, 5 bis, rue Guinaud,
F-78100 Saint Germain En Laye (FR)
Inventeur: Jorale, Marie-Françoise, 2, rue de la Renée,
F-92410 Villa D'Avray (FR)
Inventeur: Lallemand, Jacques, 84, 86, Boulevard Félix
Faure, F-93300 Aubervilliers (FR)

Etats contractants désignés: BE DE GB NL

Composés organiques à fonction nitrato utilisables comme additifs pour carburants diesel.

On décrit des composés organiques à fonction nitrato utilisables notamment comme additifs pour améliorer l'indice de cétane des carburants Diesel.

Les composés considérés répondent à la formule générale:



dans laquelle R représente un radical alkyle, linéaire ou ramifié, de 6 à 20 atomes de carbone, ou un radical aryle substitué, X est un atome d'hydrogène ou un groupe méthyle et n peut prendre une valeur de 1 jusqu'à environ 15.

Ces composés, ajoutés aux carburants pour moteurs Diesel, par exemple à une concentration de 0,01 à 3% en poids, améliorent l'indice de cétane et permettent le maintien de la propreté des systèmes d'alimentation.

L'invention concerne des composés organiques à fonction nitrato, utilisables principalement comme additifs pour améliorer l'indice de cétane des carburants pour moteurs Diesel et leur aptitude à maintenir propres les systèmes d'injection de ces moteurs.

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Le développement rapide d'unités de conversion des fractions lourdes (craquage catalytique, visco-réduction, cokage) fournit des gaz et des essences facilement valorisables, mais également des coupes moyennes (Light Cycle Oil ou L.C.O.) qui ne peuvent, dans un proche avenir, trouver d'autres débouchés que celui consistant à les incorporer dans le pool gazole. On utilise d'ailleurs déjà actuellement en Europe et en particulier en France des gazoles renfermant des proportions variables, mais notables, (5 à 30 %) de L.C.O.

Ces produits se caractérisent surtout par un faible indice de cétane (en général d'environ 40 à 48), une teneur relativement élevée en aromatiques et une tendance à la formation de dépôts à température élevée.

Sur les véhicules à moteur Diesel et plus particulièrement sur ceux qui sont équipés de moteurs à injection indirecte (avec préchambre), les gazoles renfermant des effluents de craquage entraînent une forte émission de bruit, surtout lors des phases de démarrage et de mise en action. Ces inconvénients sont liés directement à l'indice de cétane faible que présentent ces produits.

D'autre part, ces gazoles forment des dépôts sur les aiguilles d'injecteur de moteurs à préchambre, et dans les orifices d'injecteur des moteurs à injection directe. Il n'est plus possible dans ces conditions de maîtriser le débit de carburant injecté en fonction du temps, et l'on constate :

- une grande difficulté, voire une impossibilité, à obtenir un compromis rendement-pollution satisfaisant ;
- un fonctionnement erratique au ralenti et à faible charge avec émission de produits partiellement imbrûlés (fumées bleues, aldéhydes, oxyde de carbone, etc).

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Ces types d'inconvénients concernent non seulement les gazoles de cra-

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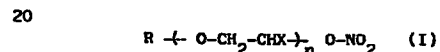
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quage, mais aussi ceux obtenus par distillation directe de pétroles bruts à caractère aromatique (Nigéria par exemple).

Pour améliorer l'indice de cétane et le comportement des gazoles, il a été proposé dans l'art antérieur d'utiliser des additifs nitrates d'alkyle, du type nitrate d'isoamyle, d'hexyle ou d'isooctyle, à une dose moyenne de l'ordre de 2000 ppm. Certains produits de cette famille sont commercialisés par la Société Ethyl sous le nom de DII (Diesel Ignition Improvers).

On a maintenant découvert de nouveaux composés à fonction nitrate agissant comme additifs d'amélioration de l'indice de cétane des carburants Diesel et qui présentent en outre des propriétés détergentes vis-à-vis des dispositifs d'injection des moteurs Diesel. Ils permettent en outre une réduction importante des fumées noires, lors des phases de fonctionnement du moteur à pleine puissance.

D'une manière générale, les composés de l'invention peuvent être définis comme répondant à la formule générale.



dans laquelle R représente un radical alkyle, linéaire ou ramifié, renfermant par exemple de 6 à 20 atomes de carbone, ou un radical aryle substitué par une ou plusieurs (par exemple 2) chaînes alkyles, renfermant par exemple de 4 à 18 atomes de carbone; X est un atome d'hydrogène ou un groupe méthyle; et la valeur de n peut aller par exemple de 1 à environ 15, de préférence de 2 à 10.

Les composés de l'invention consistent donc en des nitrates de monoalcools et en des nitrates de mono-et/ou di-alkylphénols polyéthoxylés ou polypropoxylés. Leur masse molaire peut être par exemple d'environ 200 à 1200 et de préférence de 200 à 650.

Les composés de l'invention peuvent contenir uniquement des motifs éthoxylés ou uniquement des motifs propoxylés. On envisage aussi le cas des

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composés contenant à la fois des motifs éthoxylés et propoxylés, répartis au hasard ou séquencés.

Parmi les composés selon l'invention, on considère d'une part ceux qui répondent à la formule générale (I) dans laquelle le radical R est le radical alkyle d'un monoalcool aliphatique saturé R-OH, qui peut être d'origine naturelle ou synthétique. On peut citer par exemple le n-hexanol, le n-octanol-1, l'octanol-2, l'éthyl-2 hexanol-1 (provenant du butyraldéhyde), les alcools caprylique, caprique, undécylique, laurique, tridécylique, myristique, pentadécylique, cétylique, heptadécylique, stéarylique, nonadécylique, eicosylique. On peut, bien entendu, utiliser des mélanges de deux ou plusieurs de ces alcools, tels que les octanols et nonanols provenant de la synthèse oxo, les alcools dérivés du procédé ⁶⁻⁸ ALFOL, par exemple les ALFOLS/610, 810, 1012, 1014, 1214, 1216P, 1218, 1412H, 1618 et 1620, commercialisés par la Société CONDEA. On peut encore citer les alcools qui proviennent de la réduction de coupes d'acides gras ayant un nombre d'atomes de carbone compris dans l'intervalle approprié.

Parmi les composés selon l'invention, on considère d'autre part ceux dont le radical R provient de monophénols substitués, tels que par exemple le butylphénol, l'hexylphénol, l'octylphénol, le nonylphénol, le dodécylphénol, l'hexadécylphénol ou l'octadécylphénol, dans lesquels le substituant alkyle est en général en para.

Les composés de l'invention peuvent être préparés selon différentes méthodes de nitration au moyen d'acide nitrique et de composés hydroxylés appropriés, en particulier par des méthodes mettant en oeuvre des agents de-shydratants tels que par exemple l'acide sulfurique ou l'anhydride acétique, à des températures comprises entre - 10°C et + 30°C. Les nitrates organiques ainsi obtenus présentent un excès d'acidité, qui peut être facilement neutralisé par exemple au moyen d'une base minérale (soude, potasse ou ammoniacque par exemple). Le rendement de la nitration peut atteindre par exemple 85 %.

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Les composés de l'invention sont utilisables comme additifs améliorant l'indice de cétane des carburants pour moteurs Diesel. Dans cette application, ils peuvent être ajoutés aux carburants en des proportions qui peuvent aller de 0,01 à 3 % en poids.

- 5 Les carburants Diesel peuvent consister en des coupes de distillation directe de pétroles bruts (notamment à caractère aromatique) ou en des coupes moyennes de conversion de fractions lourdes (L.C.O.), ou encore en des mélanges de coupes de ces divers types. Ils peuvent contenir en outre des proportions mineures (par exemple jusqu'à 25 % en poids) de constituants oxygénés, tels que, par exemple des alcools (notamment de l'éthanol), des cétones ou encore des éthers.

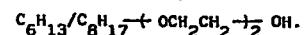
- L'addition des composés de l'invention dans les carburants Diesel, par exemple dans les proportions indiquées plus haut, permet d'en élever l'indice de cétane d'une manière significative (par exemple de 2 à 15 points), ainsi que de leur conférer une activité détergente notable, se traduisant dans la pratique par un meilleur maintien de l'état de propreté des circuits d'alimentation et des injecteurs de moteurs Diesel.

- 20 Cette action bénéfique se manifeste notamment dans les moteurs Diesel d'automobiles à injection indirecte (préchambre) dans lesquels les aiguilles d'injecteurs sont particulièrement sensibles au phénomène d'encrassement.

- 25 Les exemples suivants illustrent l'invention sans la limiter. Dans chacun des exemples 1 à 9, le mélange nitrant utilisé est constitué de 2,25 moles d'acide nitrique et de 4,5 moles d'anhydride acétique par mole de composé hydroxylé.

30 EXEMPLE 1

On utilise comme composé hydroxylé le produit d'addition d'une coupe d'alcools en C_6-C_8 sur 2 moles d'oxyde d'éthylène (ALFOL 68-2 EO vendu par la Société CONDEA) répondant à la formule



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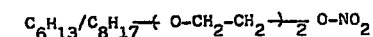
5

On introduit goutte à goutte en une heure 20,3 g de ce composé (0,1 mole) dans un mélange nitrant agité, constitué de 14,92 g d'acide nitrique fumant à 95 % et de 45,9 g d'anhydride acétique, la température étant maintenue entre - 4° C et 0° C au moyen d'un bain réfrigérant.

- On ajoute ensuite très rapidement dans le milieu réactionnel 200 cm³ d'eau glacée. La phase organique qui se sépare est lavée avec 200 cm³ d'eau ammoniacale, puis à l'eau. Après décantation, la phase organique récupérée est séchée sur Na₂SO₄ anhydro puis filtrée.

On récupère finalement 20,1 g de produit, soit un rendement réactionnel de 81 % environ.

- 15 Le spectre infra-rouge et la teneur en azote du nitrate obtenu (N = 6 %, théorie = 5,65 %) confirment la nature du produit attendu.



20 EXEMPLE 2

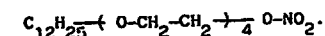
On utilise comme composé hydroxylé le produit d'addition de l'alcool laurique sur 4 moles d'oxyde d'éthylène (CENULSOL LA 40 vendu par la Société SFOS) répondant à la formule $C_{12}H_{25}-\leftarrow OCH_2CH_2-\rightarrow_4 OH$.

25

Dans des conditions opératoires identiques à celles de l'exemple 1, on effectue la nitration de 31,2 g de CENULSOL LA 40 (0,1 mole) ; On récupère finalement 34,6 g de produit, soit un rendement réactionnel de 85 % environ.

30

Le spectre infra-rouge et la teneur en azote du nitrate obtenu (N = 3,7 %, théorie = 3,44 %) confirme la nature du produit attendu.



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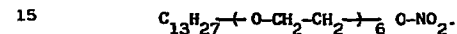
EXEMPLE 3

Le composé hydroxylé utilisé est un produit d'addition de l'alcool tridécylique sur 6 moles d'oxyde d'éthylène (SURFAROX TD 6, vendu par la Société PROTEX) répondant à la formule :

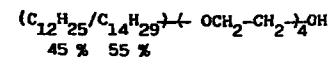


Dans des conditions opératoires identiques à celles de l'exemple 1, on effectue la nitration de 46,4 g de SURFAROX TD 6 (0,1 mole) ; on récupère 40,7 g de produit, soit un rendement réactionnel de 80 % environ.

Le spectre infra-rouge et la teneur en azote du nitrate obtenu confirment la nature du produit attendu.

EXEMPLE 4

Le composé hydroxylé utilisé est le produit d'addition d'une coupe d'alcools en $C_{12}-C_{14}$ sur 4 moles d'oxyde d'éthylène (ALFOL 1214-4 EO vendu par la Société CONDEA), représenté par la formule :



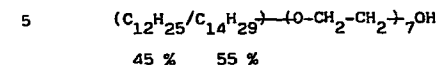
25 Dans des conditions opératoires identiques à celles de l'Exemple 1, on effectue la nitration de 37,7 g d'ALFOL 1214-4EO (0,1 mole) ; on récupère 30,4 g de produit, soit un rendement de 72 % environ.

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EXEMPLE 5

Le composé hydroxylé utilisé est un produit d'addition d'une coupe d'alcools en $C_{12}-C_{14}$ sur 7 moles d'oxyde d'éthylène (ALFOL 1214-7EO vendu par la Société CONDEA) représenté par la formule :

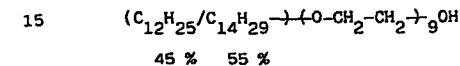


La nitration de 50,9 g d'ALFOL 1214-7EO (0,1 mole) fournit 43,2 g de produit, soit un rendement de 78 % environ.

10

EXEMPLE 6

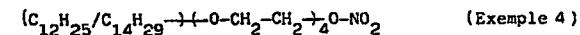
Le composé hydroxylé utilisé est un produit d'addition d'une coupe d'alcools en $C_{12}-C_{14}$ sur 9 moles d'oxyde d'éthylène (ALFOL - 1214-9 EO vendu par la Société CONDEA) représenté par la formule :



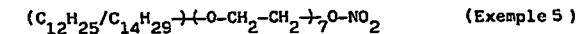
La nitration de 59,7 g d'ALFOL - 1214 -9EO (0,1 mole, fournit 52,6 g de produit, ce qui correspond à un rendement d'environ 82 %.

20

Les spectres infra-rouge et les teneurs en azote des nitrates obtenus dans les exemples 4, 5 et 6, confirment la nature des produits attendus, à savoir :



25 45 % 55 %

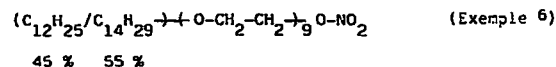


45 % 55 %

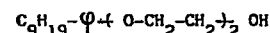
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EXEMPLE 7

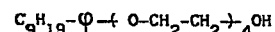
5 Le composé hydroxylé utilisé est un produit d'addition du nonylphénol sur 2 moles d'oxyde d'éthylène (CEMULSOL NP 2 vendu par la Société SFOS) représenté par la formule :



10 La nitration de 30,9 g de CEMULSOL NP 2 (0,1 mole), fournit 30,7 g de produit, ce qui correspond à un rendement d'environ 87 %.

EXEMPLE 8

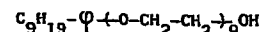
15 Le composé hydroxylé utilisé est un produit d'addition du nonylphénol sur 4 moles d'oxyde d'éthylène (CEMULSOL NP 4 vendu par la Société SFOS) représenté par la formule :



20 A partir de 39,7 g de CEMULSOL NP 4 (0,1 mole), on obtient 33,6 g de produit, soit un rendement de 76 % environ.

EXEMPLE 9

25 Le composé hydroxylé utilisé est un produit d'addition du nonylphénol sur 9 moles d'oxyde d'éthylène (CEMULSOL NP 9 vendu par la Société SFOS) représenté par la formule :

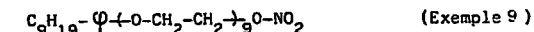
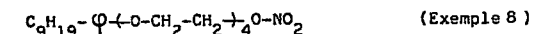
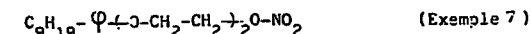


30 A partir de 61,7 g de CEMULSOL NP 9 (0,1 mole), on obtient 47,7 g de produit, soit un rendement de 72 % environ.

Les spectres infra-rouge et les teneurs en azote des nitrates obtenus dans les Exemples 7, 8 et 9 confirment la nature des produits attendus, à savoir :

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EXEMPLE 10

10 La nitration de CEMULSOL LA 40, décrit dans d'Exemple 1, est de nouveau réalisée en utilisant l'acide sulfurique comme agent de déshydratation le mélange nitrant étant alors composé de 2,25 moles d'acide nitrique et de 1 mole d'acide sulfurique à 98 %.

15 Le rendement réactionnel observé dans ces conditions est voisin de celui mesuré en présence d'anhydride acétique, et le spectre infra-rouge ainsi que la teneur en azote du produit obtenu confirment la nature du produit attendu.

TESTS SUR LES PRODUITS

On détermine les divers effets sur les gazoles des produits préparés comme décrit dans les Exemples 1 à 10.

20

TEST A

25 L'aptitude des nitrates de l'invention à augmenter l'indice de cétane (noté I.C. et déterminé selon la procédure ASTM D-613) des gazoles est mesurée, en comparaison avec des additifs commerciaux, dans un carburant constitué d'un mélange de 80 % de gazole de distillation directe et de 20 % de gazole de craquage catalytique. Les résultats obtenus à différentes concentrations exprimées en ppm poids d'azote d'origine nitrate, sont mentionnés dans le tableau I ci-après.

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TABEAU I

	ADDITIF	ppm d'azote nitrate	T.C.
	Néant	-	41
5	Nitrate d'octyle (additif commercial)	50 100 200 500	40 41,5 43,3 44,3
	$C_6H_{13}/C_8H_{17}-(OCH_2-CH_2)_2-O-NO_2$ (produit de l'exemple 1)	50 100 200 500	41 42 44 47
	$C_{12}H_{25}-(O-CH_2-CH_2)_4-O-NO_2$ (Produit de l'exemple 2)	50 100 200 500	45,5 46,5 48 54,5
10	$C_{13}H_{27}-(O-CH_2-CH_2)_6-O-NO_2$ (Produit de l'exemple 3)	50 100 200 500	44,5 45,9 47,7 49,2
	$(C_{12}H_{25}/C_{14}H_{29})_2-(O-CH_2-CH_2)_4-O-NO_2$ 45 % 55 % (produit de l'exemple 4)	50 100 200 500	46,5 47,8 49,8 54
15	$C_9H_{19}-(O-CH_2-CH_2)_2-O-NO_2$ (Produit de l'exemple 7)	50 100 200 500	46 45,3 45 47,9

Les résultats obtenus montrent qu'à nombre de fonctions nitrates identique, les nitrates des exemples 1 à 4 et 7 ont une aptitude à augmenter l'indice de cétane du gazole sensiblement plus grande que celle d'un nitrate commercial.

TEST B

L'aptitude des nitrates de l'invention à diminuer la tension superficielle du gazole (propriété détergente) est évaluée par mesure de la tension interfaciale entre le gazole additivé et l'eau par la méthode de la goutte pendante.

Cette méthode consiste à photographier le profil méridien d'une goutte de gazole dans l'eau ; l'interprétation mathématique du profil de cette goutte permet, connaissant la différence de densité des liquides, de mesurer la tension interfaciale. Cette méthode a été décrite notamment par S. FORDAM dans Proc. of the Roy. Soc. of London A vol. 194, P 1 (1948) et par E. LEFEBVRE du PREY. dans REVUE INSTITUT FRANCAIS DU PETROLE, XXIV - 6, P 701 (1969). On a utilisé le même mélange de gazoles que dans le Test A.

15

Les résultats obtenus avec un additif commercial et des additifs de l'invention à différentes concentrations sont mentionnés dans le Tableau II ci-après.

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- TABLEAU II -

	Additif	ppm d'Additif	Tension superficielle mesurée (Newton 10 ⁻³ /m)
5	Néant	-	22,2
	Nitrate d'isoamyle (additif commercial)	1 000 2 000 3 000	19,9 21 21
10	C ₁₂ H ₂₅ -(O-CH ₂ -CH ₂) ₄ O-NO ₂ (produit de l'exemple 2)	1 000 2 000 3 000	15,2 13,3 10,9
15	C ₁₃ H ₂₇ -(O-CH ₂ -CH ₂) ₆ O-NO ₂ (produit de l'exemple 3)	1 000 2 000 3 000	11,3 9 6,5
	(C ₁₂ H ₂₅ /C ₁₄ H ₂₉)-(O-CH ₂ -CH ₂) ₄ O-NO ₂ 45 % 55 % (produit de l'exemple 4)	1 000 2 000 3 000	11,8 10 8,2
20	C ₉ H ₁₉ -φ-(O-CH ₂ -CH ₂) ₂ O-NO ₂ (produits de l'exemple 7)	1 000 2 000 3 000	20,1 19 18,3

Les résultats obtenus montrent que les propriétés tensio-actives des ni-

25 rates de l'invention, notamment les nitrates d'alcools en C₁₂, C₁₃ et C₁₂, C₁₄ éthoxylés, sont très nettement supérieures à celles d'un additif "pro-cétane" commercial.

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TEST C

On détermine l'aptitude des produits de l'invention à supprimer les inconvénients liés à l'encrassement des systèmes d'injection.

On alimente un véhicule du type voiture particulière avec un gazole ren-
5 fermant 78 % d'une coupe pétrolière de distillation directe et 22 % de L.C.O. Le véhicule est disposé sur un chassis dynamométrique et effectue un parcours d'environ 2500 km selon un cycle comportant des phases à vitesse stabilisée à 50 km/h. Avant et après ce parcours, on effectue des cycles urbains du type ECE (Le cycle ECE est utilisé en Europe pour
10 mesurer les émissions de polluants et la consommation de carburant des véhicules).

Les essais ont été réalisés avec le gazole seul et avec le même gazole contenant 2000 ppm de l'additif de l'Exemple 4.

15

Les résultats relatifs aux émissions de polluants sont présentés dans le Tableau III ci-après.

- TABLEAU III -

20

	Gazole	Gazole de Réf. (sans additif)		Gazole + 2000 ppm du nitrate de l'Exemple 4	
25	Kilométrage réalisé avec un lot donné d'injecteurs	0	2500 km	0	2500 km
	Emissions selon le cycle ECE :				
	CO (g/essai)	6,4	10,8	6,6	6,8
30	Hydrocarbures "				
	Imbrûlés	1,6	6,9	1,4	1,3
	Particules "	0,4	1,5	0,5	0,6

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Ces résultats montrent, pour le gazole non additivé, un accroissement très net des taux de polluants entre le début de l'essai et après 2500 km. On observe corrélativement une détérioration très importante du fonctionnement au ralenti et à faible charge (bruit, régime instable).

5

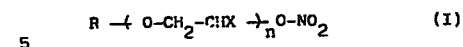
Avec le gazole additivé, l'évolution des taux de polluants entre le début de l'essai et après 2500 km est très faible. En outre le moteur fonctionne régulièrement et sans bruit anormal.

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REVENDICATIONS

1. Composé organique à fonction nitrate, caractérisé en ce qu'il répond à la formule générale :



dans laquelle R représente un radical alkyle, linéaire ou ramifié, de 6 à 20 atomes de carbone ou un radical aryle, substitué par une ou plusieurs chaînes alkyles de 4 à 18 atomes de carbone ; X est un atome d'hydrogène ou un groupe méthyle et n est un nombre entier de 1 à 15.

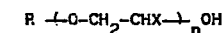
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2. Composé organique selon la revendication 1, caractérisé en ce que, dans la formule (I), n est un nombre entier de 2 à 10.

3. Composé organique selon la revendication 1 ou 2, caractérisé en ce qu'il comprend, dans la même molécule, des groupements $-O-CH_2-CHX-$ dans lesquels X est un atome d'hydrogène, et des groupements $-O-CH_2-CHX-$ dans lesquels X est un radical méthyle.

4. Composition caractérisée en ce qu'elle consiste en un mélange de composés selon l'une des revendications 1 à 3, dans lesquels les radicaux alkyles R diffèrent par leur nombre d'atomes de carbone.

5. Procédé de préparation d'un composé organique selon l'une des revendications 1 à 3 ou d'une composition selon la revendication 4, caractérisé en ce que l'on réalise la nitration d'au moins un composé hydroxylé répondant à la formule générale :



au moyen d'acide nitrique à une température de $-10^{\circ}C$ à $+30^{\circ}C$, et en présence d'un agent déshydratant choisi parmi l'anhydride acétique et l'acide sulfurique, l'excès d'acidité des produits obtenus étant neutralisé au moyen d'une base minérale.

6. Composition de carburant pour moteurs Diesel, caractérisée en ce

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qu'elle contient une proportion majeure d'au moins un gazole et une proportion mineure, suffisante pour en élever l'indice de cétane, d'au moins un composé selon l'une des revendications 1 à 3.

5 7. Composition de carburant pour moteurs Diesel selon la revendication 6, caractérisée en ce que la proportion dudit (desdits) composé(s) est de 0,01 à 3 % en poids par rapport au(x) gazole(s).

8. Composition de carburant selon l'une des revendications 6 et 7, caractérisée en ce que ledit gazole comprend au moins une coupe moyenne provenant de la conversion de fractions lourdes de pétrole.

9. Composition de carburant selon l'une des revendications 6 à 8, caractérisée en ce que ledit gazole comprend au moins une coupe de distillation directe de pétrole brut à caractère aromatique.

10. Composition de carburant selon l'une des revendications 6 à 9, caractérisée en ce que ledit gazole contient en outre une proportion mineure d'au moins un composé oxygéné choisi parmi les alcools, les cétones et les éthers.



Office européen
des brevets

RAPPORT DE RECHERCHE EUROPEENNE

0157684

Numéro de la demande

EP 85 40 0499

DOCUMENTS CONSIDERES COMME PERTINENTS			
Catégorie	Citation du document avec indication, en cas de besoin, des parties pertinentes	Revendication concernée	CLASSEMENT DE LA DEMANDE (int. Cl. 4)
X	US-A-2 742 492 (C.C. HARVEN) * Colonne 1, lignes 15-27; colonne 2, lignes 32-36, 48-53 et 57-61 *	1, 5, 6	C 07 C 77/02 C 07 C 76/04 C 10 L 1/22
Y	DE-A-2 039 609 (COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH) * Page 1; page 2, alinéa 2 *	1, 5, 6	
			DOMAINES TECHNIQUES RECHERCHES (int. Cl. 4)
			C 07 C 77/00 C 07 C 76/00
Le présent rapport de recherche a été établi pour toutes les revendications			
Lieu de la recherche LA HAYE		Date d'achèvement de la recherche 21-05-1985	Examineur KINZINGER J.M.
CATEGORIE DES DOCUMENTS CITES			
X : particulièrement pertinent à lui seul Y : particulièrement pertinent en combinaison avec un autre document de la même catégorie A : arrière-plan technologique O : divulgation non-écrite P : document intermédiaire		T : théorie ou principe à la base de l'invention E : document de brevet antérieur, mais publié à la date de dépôt ou après cette date D : cité dans la demande L : cité pour d'autres raisons & : membre de la même famille, document correspondant	

12 EUROPEAN PATENT APPLICATION

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64 Microemulsion diesel fuel compositions and method of use.

57 The present invention relates to translucent and thermodynamically stable fuel compositions having improved combustion efficiency and reduced smoke, particulate, CO, and NOx emissions. The fuel compositions comprise, for example, a diesel fuel, water, or an aqueous solution of a low molecular weight alcohol and/or a water-soluble reagent, and a surfactant system which comprises a balanced blend of one or more hydrophilic surfactants and one or more lipophilic surfactants, wherein the diesel fuel composition can contain as high as 30 weight percent of aqueous phase with an aqueous phase/surfactant ratio at least 2/1. The surfactant system may contain, in addition to the hydrophilic and lipophilic surfactants, cosurfactants and polar organic solvents. The reagent solution comprises aqueous solutions of an additive selected from the group consisting of inorganic oxidizing agents, low molecular weight polar organic oxidizing agents, and nitrogen oxide-containing compounds which act as cetane improvers and/or combustion modifiers. These additives offset the well-known loss in cetane number and/or the ignition delay caused by dispersed or microemulsified water and eliminate the need to change engine operating parameters.

EP 0 475 620 A2

The present invention relates to novel microemulsion compositions which are transparent and thermodynamically stable fluids useful in reducing diesel exhaust emissions.

There is a wide variety of micro emulsion fuel compositions known in the art. A disadvantage of these has been a lack of stability under conditions to which the fuels have been exposed. Prior compositions, for example, have been unstable and have tended to de-emulsify at high and at low temperatures; high temperature de-emulsification has been a special problem. Further, the addition of even very small amounts of salt as by exposure to salt-containing air or water has caused severe de-emulsification problems in prior formulations that did not contain alcohols. Another disadvantage of prior microemulsion fuel compositions has been the high concentrations of surfactants required to form the microemulsions. Prior inventions, generally, employed one or more parts of surfactant per part of solubilized water.

The microemulsions of the instant invention seek to overcome the foregoing deficiencies by providing improved temperature and salt stability and employing lower concentrations of surfactants.

The present invention provides a translucent and thermodynamically stable fuel compositions having improved combustion efficiency and reduced smoke, particulate, CO, and NOx emissions. The fuel compositions comprise for example, diesel fuel, water or an aqueous solution of a low molecular weight alcohol and/or a water-soluble reagent, and a surfactant system which comprises a balanced blend of one or more hydrophilic surfactants and one or more lipophilic surfactants, wherein the diesel fuel composition can contain as high as 30 weight percent of aqueous phase with an aqueous phase/surfactant ratio at least 2/1.

The present translucent and thermodynamically stable microemulsion compositions of this invention comprise a hydrocarbon fuel such as gasoline, jet fuel, or preferably diesel fuel; about 1 to about 30 weight percent, more preferably about 2 to about 20 weight percent, and most preferably about 2 to about 15 weight percent of an aqueous composition comprising water, from 0 to 30 weight percent based on the amount of water of a 1 to 3 carbon alkanol and less than 20 weight percent based on the amount of water of one or more additives selected from the group consisting of ashless inorganic oxidizing agents, low molecular weight polar organic oxidizing agents, and nitrogen oxide-containing compounds wherein the additive is preferably selected from the group consisting of: ammonium nitrate, ammonium nitrite, hydrogen peroxide, ammonium hypochlorite, ammonium chlorite, ammonium perchlorate, ammonium chlorate, perchloric acid, chlorous acid, hypochlorous acid, ammonium hypobromite, ammonium bromate, hypobromous acid, bromic acid, ammonium hypiodite, ammonium periodate, hypiodous acid, iodic acid, periodic acid, 2,4 dinitrophenyl hydrazine, 2,5 dinitrophenol, 2,6 dinitrophenol, 2,4 dinitroresorcinol, nitroguanidine, 3 nitro-1,2,4-triazole, 4 nitro imidazole, picric acid, cumene hydroperoxide, cyanuric acid, nitroglycerin, nitrobenzene, trinitrotoluene, and mixtures thereof; and, about 0.5 to about 15 weight percent, more preferably about 1 to about 10 weight percent and most preferably about 1 to about 5 weight percent of a surfactant system which comprises a balanced blend of one or more hydrophilic surfactants and one or more lipophilic surfactants wherein the ratio of aqueous composition/surfactant system is preferably at least 2/1.

It is well-known in the art that dispersions of water and/or one or two carbon alkanols in diesel fuel reduce harmful diesel emissions such as smoke, soot, particulates, and NO_x. It is also well-known that debits associated with water and alkanols in diesel fuels entail a severe reduction in cetane number and a marked ignition delay often requiring engine and/or operating parameter modification such as advanced ignition timing or the installation of glow plugs. The novel compositions of the instant invention, by the incorporation into the aqueous composition of an oxidizing and/or nitrogenous reagent, offset these debits while still retaining the advantages in emissions reduction.

In the practice of the present invention, at least one hydrophilic surfactant and at least one lipophilic surfactant are selected and their ratio adjusted with respect to their combined hydrophilic and lipophilic properties such that they form with the fuel and the aqueous composition a single phase, translucent microemulsion. The hydrophilic surfactant(s) is defined by a set of operations wherein a blend of equal volumes of fuel and aqueous composition with 2 grams of said surfactant per deciliter of liquids forms a lower phase microemulsion at 20°C such that the volume ratio of fuel (oil) to surfactant (Vo/Vs) in the microemulsion phase is at least 0.5, preferably greater than 1 and more preferably greater than 2. The term "lower phase" microemulsion is descriptive in context since it means that the aforementioned system consisting of the hydrophilic surfactant and equal volumes of fuel and aqueous composition separates into an aqueous lower phase containing most of the surfactant in equilibrium with an excess fuel (oil) phase which is essentially surfactant-free.

The hydrophilic surfactant which is defined by the above properties includes, but is not limited to, the alkyl carboxylic and alkylaryl sulfonic acid salts wherein the alkyl group is a C₆ to C₁₈ linear, branched or bifurcated structure, the aryl group is selected from benzene, toluene, orthoxylene, and naphthalene, and the salt is a salt of an alkali metal, ammonia, or alkanol amine. Also included, and preferred are the ethoxylated alkyl-phenols. Most preferred are the ethoxylated C₁₂-C₁₈ alkyl ammonium salts of C₇-C₂₄ alkyl carboxylic and alkylaryl sulfonic acids containing 6 or more ethylene oxide (hereinafter EO) groups, wherein the alkyl and aryl

Representative examples of hydrophilic alkyl carboxylic and alkylaryl sulfonic acid salts include monoethanol ammonium laurate, ammonium palmitate, diethanol ammonium stearate, monoethanol ammonium myrtil xylene sulfonate, sodium dodecyl benzene sulfonate, ammonium tetradecyl benzene sulfonate, diethanol ammonium hexadecyl benzene sulfonate, and sodium dodecyl naphthalene sulfonate. Preferred hydrophilic carboxylic acid salts include monoethanol ammonium oleate, penta-, deca-, and hexadeca-ethoxy octadecyl ammonium oleate. Preferred hydrophilic sulfonic acid salts include penta- and deca-ethoxy octadecyl ammonium benzene sulfonate (designated C₁₂BS-E18-5 and C₁₂BS-E18-10, respectively), heptaethoxy octadecyl ammonium dodecyl o-xylene sulfonate (designated C₂₀XS-E18-7) and decaethoxy octadecyl ammonium dodecyl ortho xylene sulfonate (designated C₁₂XS-E18-10). The ethoxylated alkyl amines used in preparing the ethoxylated alkyl ammonium salts of alkyl aryl sulfonic acids can be obtained from Exxon Chemical. Performance Products, Tomah Products.

Representative hydrophilic ethoxylated alkyl phenols include Igepal DM 710, Igepal DM 730, and Igepal DM 880 available from GAF which are chemically dinonyl phenols ethoxylated with 15, 24, and 49 moles of EO, respectively. Preferred is Igepal DM 530 which is dinonyl phenol ethoxylated with 9 moles of ethylene oxide. Other suitable ethoxylated alkyl phenols include Tritons X100, X102, and X114 available from Rohm and Haas of Philadelphia, Pa., and Igepals CO 610, 630, 660, 710, 720, 730, 850, and 880 which are chemically mono-*o*-cyl or nonyl phenols ethoxylated with from 8 to 30 EO.

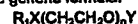
The lipophilic surfactant for purposes of this invention is a surfactant having the properties of providing at 2 g/dl concentration in equal volumes of fuel and aqueous composition an upper phase microemulsion at 20°C such that the volume ratio of water to surfactant (Vw/Vs) in the microemulsion phase is at least 0.5, preferably greater than 1 and most preferably greater than 2. The term "upper phase" microemulsion as used in defining the lipophilic surfactant ingredient means that the system consisting of the surfactant in equal volumes of fuel and aqueous composition separates into a surfactant containing oil upper phase in equilibrium with an excess aqueous phase which is essentially surfactant free.

The lipophile having been defined by the above properties includes, but is not limited to, the ethoxylated alkyl phenols. Also included and preferred are the alkyl and alkaryl sulfonic acid salts wherein the alkyl group is a C_{12} to C_{24} linear, branched, or bilinear structure, the aryl group is selected from benzene, toluene, orthoxytylene, and naphthalene; and the salt is a salt of an alkali metal, ammonia or alkanoil amine. More preferred are the ethoxylated C_{12} - C_{18} alkyl ammonium salts of C_8 - C_{24} alkyl carboxylic and alkaryl sulfonic acids containing less than six EO groups, wherein the alkyl and aryl groups are as previously defined above.

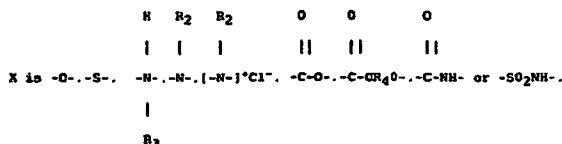
Representative examples of lipophilic alkyl aryl sulfonates include monoethanol ammonium dodecyl *o*-xylene sulfonate, sodium tetradecyl *o*-xylene sulfonate, sodium hexadecyl *o*-xylene sulfonate, diethanol ammonium pentadecyl *o*-xylene sulfonate, triethanol ammonium octadecyl *o*-xylene sulfonate (prepared from penta and hexa propylene), sodium octapropylene benzene sulfonate, sodium tetracosyl toluene sulfonate, and various high molecular weight petroleum sulfonates. Preferred are the sodium and monoethanol ammonium salts of dodecyl *o*-xylene sulfonic acid. Most preferred are di-ethoxy octadecyl ammonium oleate, di- and penta-ethoxy octadecyl ammonium dodecyl *o*-xylene sulfonate (designated E18-2 oleate, C₁₂XS-E18-2 and C₁₂XS-E18-5, respectively).

Representative lipophilic ethoxylated alkyl phenols include Igepals CO 210 and CO 430 which are nonyl phenols containing 1.5 and 4 moles of EO, respectively, and Tritons X15 and X35 which are octyl phenols containing 1 and 3 moles of EO, respectively.

The present invention is not confined to the use of the aforementioned ethoxylated alkyl phenols but includes other ethoxylated surfactants of the generic formula:



wherein R₁ is an alkyl or mono or di-alkyl aryl group containing 8 to 30 carbon atoms,



and Y is $-H$, $-SO_2-M^+$ or $-(PO_3H)-M^+$ wherein M^+ is an inorganic or ammonium cation including alkyl substituted ammonium cations; R_2 is an alkyl group containing 1 to 20 carbon atoms or a polyethoxy ether group containing

from 1 to 30 ($\text{CH}_2\text{CH}_2\text{O}$) groups; R_3 is H or an alkyl group containing 1 to 3 carbon atoms; R_4 is a polyhydroxy group derived from glycerol, glycols, sorbitol, or various sugars; and n is an integer of from 1 to 30.

The above ethoxylated alkyl phenols may be blended with an alkali metal, ammonium, alkyl ammonium, alkanol ammonium, or ethoxylated alkyl ammonium salt of an alkyl or alkyl aryl sulfonic acid of the generic formula:



wherein R is an alkyl or alkyl benzene group containing 8 to 30 carbon atoms in the alkyl chain and the benzene ring may be additionally substituted with one or two alkyl groups containing 1 to 3 carbon atoms each to provide the balanced blend of surfactants. Preferred blends of ethoxylated alkyl phenols with alkyl aryl sulfonates include combinations of Igepal CM 530 or Igepal DM 710 with the sodium or monoethanol amine salt of C₁₂ o-xylene sulfonic acid.

Alternatively, ethoxylated alkyl ammonium salts of the above alkylaryl sulfonic acids containing varying degrees of ethoxylation are blended to provide the balanced blend of surfactants. Preferred blends of ethoxylated alkyl ammonium salts of alkylaryl sulfonic acids include penta-ethoxy octadecyl ammonium dodecyl benzene sulfonate combined with hepta-ethoxy octadecyl ammonium dodecyl benzene sulfonate and di-ethoxy cocoa ammonium dodecyl o-xylene sulfonate with deca-ethoxy octadecyl ammonium dodecyl oxyline sulfonate. Most preferred is the blend of penta-ethoxy octadecyl ammonium dodecyl o-xylene sulfonate with hepta- or deca-ethoxy octadecyl ammonium dodecyl o-xylene sulfonate, i.e., a blend of C₁₂XS-E18-5 with C₁₂XS-E18-10.

Alternatively, alkali metal, ammonium, alkyl ammonium, alkanol ammonium or ethoxylated alkyl ammonium salts of alkyl carboxylic acids of the generic formula:

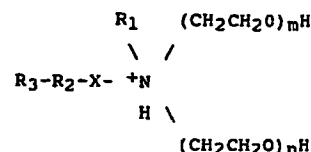


wherein R' is an alkyl group of 12 to 20 carbon atoms may be substituted for the sulfonic acid salts described above. These salts may be blended with ethoxylated alkyl phenols. Alternatively, ethoxylated alkyl ammonium salts of the above alkyl carboxylic acids containing varying degrees of ethoxylation are blended together to provide the balanced blend of surfactants. Most preferred is a blend of penta-ethoxy octadecyl ammonium oleate with deca-ethoxy octadecyl ammonium oleate, i.e. a blend of E18-5 oleate with E18-10 oleate.

Under certain circumstances, up to 20, generally 2 to 10, weight percent of a cosurfactant is included in the surfactant blend to improve the solubility of the surfactant in the fuel and reduce the viscosity of the microemulsion diesel fuel composition. The cosurfactants are of the class of alkylene glycol monoalkyl ethers, C_4 to C_6 alkanols and mixtures thereof. Representative cosurfactants include ethers such as ethylene glycol monopropyl ether, methylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, diethyl glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol *n*-butyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether and tripropylene glycol monomethyl ether, and alkanols which include straight and branched chain members such as butanol and pentanol. Of the alkanols, tertiarv amyl alcohol (TAA) is preferred. Of the ethers, ethylene glycol monobutyl ether is preferred.

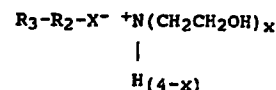
It is understood that when using a cosurfactant, the ratio of the surfactants may have to be readjusted for changes in phase behavior brought about by the addition of cosurfactant. It is also understood that the weight ratio of hydrophilic to lipophilic surfactants may have to be readjusted for changes in phase behavior brought about by different aqueous reagents and variations in their concentration. For example, an increase in the concentration of the aqueous reagent ammonium nitrate, requires an increase in the ratio of hydrophilic to lipophilic surfactants. Likewise changes in the composition of the fuel necessitate readjustment of the surfactant ratio. For example, a higher concentration of aromatics in the fuel requires an increase in the ratio of hydrophilic to lipophilic surfactants. It is also understood that when a change in surfactant ratio is inadequate to compensate for a given change in the fuel or aqueous composition, choice of a more (or less) hydrophilic surfactant pair (e.g. more (or less) ethoxylation) may be required. These points will be made clear by the examples cited below. The preferred surfactant blends of the instant invention provide a marked improvement over the art by solubilizing much more aqueous phase per unit of surfactant than disclosed in the art. The art discloses diesel fuel microemulsions containing less than 2 volumes of water per volume of surfactant. The examples cited below disclose compositions with greater than 2 up to 4 volumes of aqueous phase per volume of surfactant.

The most preferred surfactants for the instant invention are selected from Group 1, having the generic formula:



where R_1 and R_3 are alkyl groups which may be paraffinic or olefinic and may contain 8 to 24 carbon atoms. R_2 is a methyl group or a benzene, toluene, or xylene ring, $m+n=2$ to 20 and X^- is $-COO^-$ or SO_3^- . Non-limiting representative examples of Group 1 surfactants are ethoxylated octadecyl ammonium dodecyl benzene sulfonate ($C_{12}BS-E18-(n+m)$ where $R_1 = C_{18}H_{37}$, $R_3 = C_{12}H_{25}$, $R_2 = C_6H_5$, and $X^- = SO_3^-$); ethoxylated octadecyl ammonium dodecyl xylene sulfonate ($C_{12}XS-E18-(n+m)$ where $R_1 = C_{18}H_{37}$, $R_3 = C_{12}H_{25}$, $R_2 = (CH_3)_2C_6H_4$, and $X^- = SO_3^-$) and ethoxylated octadecyl ammonium oleate ($E18-(n+m)$ oleate where $R_1 = C_{18}H_{37}$, $R_3 = R_2 = CH_3(CH_2)_7CH=CH(CH_2)_7$ and $X^- = COO^-$).

Other most preferred surfactants are selected from Group 2, having the generic formula:



where R_3 and R_2 are defined as in Group 1 and $x=3$. Non-limiting representative examples of Group 2 surfactants are monoethanol ammonium dodecyl benzene sulfonate ($C_{12}BS-MEA$), monoethanol ammonium dodecyl xylene sulfonate ($C_{12}XS-MEA$), diethanol ammonium pentadecyl benzene sulfonate ($C_{15}XSDEA$), ammonium oleate and monoethanol ammonium oleate.

We have discovered that it is often advantageous to blend a surfactant(s) from Group 1 with a surfactant(s) from Group 2 to form the balanced blend of hydrophilic and lipophilic surfactant(s). We have discovered that surfactants from Group 1 become more lipophilic with increasing temperature while those from Group 2 become more hydrophilic with increasing temperature. We have also discovered that blends of surfactants from Group 1 with those from Group 2 form microemulsions which are more stable to phase separation over a broad temperature range than microemulsions hitherto found in the art. This reduction in temperature sensitivity is a highly desirable feature of our most preferred diesel fuel microemulsions. Diesel fuel, when stored over a period of time, may be subjected to wide temperature fluctuations. Conventional microemulsified diesel fuel phase separates under these conditions while our most preferred fuel microemulsion compositions remain stable.

Example I

Preparation of Anionic-Ethoxy Cationic Complexes

One hundred grams of the alkyl carboxylic or alkyl aryl sulfonic acid is weighed into a wide mouth jar. An appropriate weight of the ethoxylated alkyl amine, as listed in Table I, is added and stirred vigorously while warm from the heat of neutralization. Properties, neutralization weights, and chemical suppliers are listed in Table I.

TABLE I

Preparation of Anionic-Ethoxy Cationic Complexes

Component	Average	wt. %	Equ/100g
	Mol. wt.	Actives	
Oleic acid	282	100	0.354
$C_{12}BSH$ (Vista SA 597)	326	-98	0.336 ¹
$C_{12}XSH$ (ESSAF SA 149)	354	-81	0.226 ¹
$C_{18}N(EO)_2$ (Tomah E18-2) ^a	357	-98	0.275
$C_{18}N(EO)_5$ (Tomah E18-5) ^b	489	-98	0.200
$C_{18}N(EO)_{10}$ (Tomah E18-10) ^c	709	-98	0.138
$C_{18}N(EO)_{15}$ (Tomah E18-15) ^d	929	-98	0.105
MEA (mono ethanol amine)	61	100	1.639

Weight(g) of Amine/100 g Acid

Amine	$C_{12}XSH$	$C_{12}BSH$	Oleic Acid
MEA	13.8	20.5	21.6
E18-2	82.3	122.4	128.0
E18-5	112.8	167.7	176.6
E18-10	163.5	243.1	256.1
E18-15	214.2	318.5	335.6

¹ By titration

² Direct replacements: a) Akzo Ethomeen 18/12

b) Ethomeen 18/15

c) Ethomeen 18/20

d) Ethomeen 18/25

Example II

Microemulsion Preparation

Microemulsions were prepared as follows. The surfactants were weighed into a 16 x 125 mm flat bottom tube fitted with a teflon-lined cap. A total of 15 ml of diesel fuel and water were added. The tubes were shaken and heated -30 minutes to 1 hour at 60-70°C. They were then tumbled overnight to 2 days on an automated tumbler. Most systems, particularly those made with the alkyl benzene sulfonates, did not clear at room temperature after 2 days of tumbling. They could be made to clear in most cases by temperature cycling 2 or 3 times from 70°C to 0°C. On storage at room temperature, clarity improved with age for the systems containing the MEA soaps. Systems based solely on the $C_{12}XS$ E18-n surfactants were found to be extremely temperature sensitive and to deteriorate with age. Often systems which were initially single phase and clear, phase separated on storage at room temperature. The assumed cause was laboratory temperature fluctuations coupled with the extreme temperature sensitivity of these systems. Because of poor storage stability, blends of only

C₁₂XS E18-n surfactants were eliminated early on from further study. However, work with these surfactants did demonstrate that clear microemulsions could be prepared with 3 vol.% water and as little as 1 g/dl (~1%) surfactant. Clear single phase systems containing 5% water stabilized by 2 g/dl of the C₁₂XS E18-n surfactants were also prepared. Blends of these C₁₂XS E18-n surfactants with surfactants based on MEA (e.g. C₁₂BS-MEA or C₁₂XS-MEA) gave good stability and are described below.

Example III

Selecting and Balancing the Hydrophilic and Lipophilic Surfactant Blend

A 2 gm/dl mixture of monoethanol ammonium dodecyl benzene sulfonate (hereafter C₁₂BS-MEA) with equal volumes of Maraven diesel fuel (oil) and water forms a lower phase microemulsion at 20°C. The volume of oil solubilized per gm of surfactant (oil uptake) is greater than the most preferred design criterion for a hydrophilic surfactant of 2 ml oil/gm surfactant. A 2 gm/dl mixture of di-ethoxy octadecyl ammonium dodecyl benzene sulfonate (hereafter C₁₂BS E18-2) with equal volumes of Maraven diesel fuel and water forms an upper phase microemulsion at 20°C. The volume of water solubilized per gm of surfactant (water uptake) is greater than the most preferred design criterion for a lipophilic surfactant of 2 ml water/gm surfactant.

The combination C₁₂BS-MEA/C₁₂BS E18-2 represents a hydrophile-lipophile surfactant couple and their combined hydrophilic and lipophilic properties are varied by adjusting the weight ratio of C₁₂BS-MEA/C₁₂BS E18-2. Table II presents phase data for the C₁₂BS-MEA/C₁₂BS E18-2 surfactant couple at various water to Maraven oil ratios and total surfactant concentrations. The data were generated as follows. The surfactant concentration was fixed at, for example, 2 g per deciliter of oil and water at a water/oil ratio of 5/95. The weight fraction of C₁₂BS-MEA, the hydrophile in the surfactant couple was then varied in the range between 0.45 and 0.60. The type of microemulsion at each weight fraction of C₁₂BS-MEA was noted after equilibrium was reached. A change in microemulsion type indicated the approximate phase transition boundary between upper and single or single and lower phase microemulsions. These transition boundaries are noted in Table II. The procedure was repeated at 1.5 and 1.0 g/dl surfactant concentration and the approximate transition boundaries determined. Note that the data was developed on a series of individual equilibrated tubes, each containing the specific ratio of surfactants at the listed total surfactant concentration in water and oil at a 5/95 volume ratio. The single phase region lies between the upper and lower phase transition boundaries. The point where these phase boundaries coincide indicates the minimum surfactant concentration which will solubilize 5% water in Maraven diesel fuel; in this case, it takes somewhat more than 1 g/dl of surfactant to form a stable microemulsion. However, the proximity to the phase transition boundaries indicates that this will not be a clear system. In general, the clearest systems are found farthest from the transition boundaries, that is, in the center of the single phase region. The closer the transition boundaries, the hazier the systems located between them. Thus, maximum clarity at a given water concentration is attained at higher surfactant concentrations.

Table II presents similar phase data for the C₁₂BS-MEA/C₁₂BS E18-2 surfactants holding the water/oil volume ratio fixed at 4/96. The single phase region has broadened and at 2 g/dl surfactant extends between 0.47 and 0.59 wt. fraction of C₁₂BS-MEA compared with a range of 0.48 to 0.56 for the 5/95 water/oil system. Again the clearest systems are found in the center of the single phase region and since the 4/96 systems are farther from the phase transition boundaries than are the 5/95 systems, they are also clearer in comparison. The 4/96 water/oil systems form single phase microemulsions at surfactant concentrations somewhat below 1 g/dl. Again, these microemulsions are turbid because of their proximity to the phase transition boundaries.

The data in Table II reinforce the conclusion that higher surfactant/water ratios provide clearer microemulsions. The single phase region at a surfactant concentration of 2 g/dl for the 3/97 water/oil system extends between 0.46 and 0.60 wt. fraction C₁₂BS-MEA. Thus microemulsions in the center of this range are even farther from the transition boundaries and, therefore, clearer than those found with 5/95 or 4/96 water/oil systems. The 3/97 system forms single phase microemulsions at surfactant concentrations above 0.75 g/dl. Comparison with the 5/95 and 4/96 water/oil systems shows that for all these water/oil ratios, the minimum surfactant concentration for single phase microemulsions corresponds to a water/surfactant ratio of ~4/1.

The data in Table II illustrate the critical nature of selecting and balancing the hydrophile/lipophile surfactant blend for a given amount of water and surfactant. The data indicate that stable microemulsions can be prepared with up to 5% water with less than 1.5% surfactant. An increase in surfactant concentration permits a proportionate increase in the amount of water solubilized. These surfactants are more efficient than those found in the previous art.

TABLE II
C₁₂BS-MEA/C₁₂BS E18-2 Compositions for Single Phase

W/O Vol. Ratio	Surfactant Concn g/dl	Wt Fraction C ₁₂ BS-MEA ¹ at the	
		Upper Phase TB ²	Lower Phase TB ³
5/95	1.0	0.52	0.52
	1.5	0.50	0.54
	2.0	0.48	0.56
4/96	1.0	0.53	0.53
	1.5	0.50	0.56
	2.0	0.47	0.59
3/97	0.75	0.52	0.52
	1.0	0.50	0.54
	1.5	0.48	0.57
	2.0	0.46	0.60

1) At the indicated total surfactant concentration

2) Upper phase transition boundary U S

3) Lower phase transition boundary S L

The C₁₂XS-MEA/C₁₂XS E18-5 system, though not as extensively investigated as the C₁₂BS-MEA/C₁₂BS E18-2 system described above, provides a similar phase behavior pattern. In this case, the C₁₂XS-MEA is the hydrophile; its increasing weight fraction leads to lower phase microemulsions. Phase data obtained for three water/oil ratios at a surfactant concentration fixed at 1.5 g/dl are given in the following table.

C₁₂XS-MEA/C₁₂XS E18-5 Compositions for Single Phase

W/O Vol. Ratio	Wt. Fraction C ₁₂ XS-MEA ¹	
	UTB ²	LTB ³
5.0/95.0	0.49	0.55
4.5/95.5	0.47 (estim.)	0.57
4.0/96.0	0.44 (estim.)	0.60

- 1 At a total surfactant concentration of 1.5 g/dl.
- 2 Upper phase transition boundary: u s
- 3 Lower phase transition boundary: s l

As discussed previously, the single phase region, which lies between the upper phase transition (UTB) and the lower phase transition boundary (LTB), broadens and clarity improves with decreased water/oil ratio. The clarity of microemulsions in the center of the single phase region is somewhat better than observed with the C₁₂BS-MEA/C₁₂BS E18-2 system. In addition, the rate of equilibration is faster with the C₁₂XS-MEA/C₁₂XS E18-5 system; less temperature cycling is required and clarity is obtained sooner on ambient storage after temperature cycling.

Example IV

Microemulsion Preparation From Concentrates

In order to check whether other compositional paths to the final microemulsion might speed equilibration, we explored the use of concentrates as intermediate compositions. These concentrates were prepared by backing out oil and in some cases part of the water from the final composition. For example, the following concentrate was prepared:

Concentrate NB 14483-75A

C ₁₂ XS-MEA	3.0
C ₁₂ E18-5	12.0 wt. %
CK #90537 D.O.	25.0
Water	50.0

The surfactants were dissolved in diesel oil at room temperature and the water mixed in last. The system forms a thin, clear gel at room temperature which melts into a clear fluid on gentle warming. If 1.2 g of this concentrate is added to 14.1 ml of diesel fuel, the resulting mixture is turbid and clears slowly over a period of several hours to form a bright microemulsion. If the diesel fuel is mixed in stages with the concentrate over a period of several minutes, the final system is a clear microemulsion. This shows that equilibration rate depends on composition path as well as temperature path. It also suggests that it would be advantageous to predilute the above concentrate with some added diesel oil. With this in mind we prepared the following concentrate:

Concentrate NB 14483-76A

C ₁₂ XS-MEA	10.4
C ₁₂ XS E18-5	9.6 wt. %
CK #90537 D.O.	40.0
Water	40.0

The surfactants were dissolved in the diesel oil at room temperature and the water added last. The mixture was turbid initially but slowly cleared with mild warming (-40°C) and stirring over a period of several hours to finally form a clear amber "solution." This fluid concentrate when diluted by a factor of 10 instantly forms with little mixing a bright microemulsion containing 2 wt. % surfactant and 4% water. This microemulsion remains clear over the temperature range of -10°C (lower cloud point) to >70°C (upper cloud point) and is indefinitely stable at room temperature. It is not known at this time whether the turbidity below -10°C is due to phase separation in the microemulsion or wax precipitation from the diesel fuel.

The above concentrates have a water/surfactant volume ratio of 2/1. In an attempt to raise the water/surfactant ratio, the following concentrate was prepared:

Concentrate NB 14483-78B

C ₁₂ XS-MEA	5.78 wt. %
C ₁₂ XS E18-5	5.33
CK #90537 D.O.	55.56
Water	33.33

The water/surfactant ratio in this package is 3/1. No attempt was made to optimize the surfactant H/L ratio for the added water. Clarity was achieved by adjusting the oil/water ratio in the package. A quantity, 1.89 g of this concentrate when diluted with 8.2 g of diesel oil instantly forms a clear microemulsion containing 2% surfactant and 6% water. This microemulsion is not quite as bright as the microemulsion prepared with concentrate NB 1448376A due to the higher water content. Brightness may be improved with optimization of surfactant H/L ratio. This essay holds promise of achieving even higher water/surfactant ratios.

Example V

Ammonium Nitrate Diesel Fuel Microemulsions

In order to determine whether the loss in cetane number due to microemulsified water could be eliminated by the addition of potential cetane improvers, we initiated experiments designed to incorporate NH₄NO₃ into the microemulsified aqueous phase. Table III describes the results of our studies to incorporate up to 10 wt. % NH₄NO₃ based on water. Since the microemulsions contain 10% aqueous phase, 10% NH₄NO₃ based on water translates into a 1% NH₄NO₃ concentration overall. Based on previous results with oil-soluble cetane improvers such as octyl nitrate, 0.1% or 1000 ppm NH₄NO₃ was thought to be an effective level for cetane improvement.

Table III describes microemulsion phase behavior with varying surfactant hydrophile/lipophile (H/L) ratio and salinity. H/L ratio depends on the average degree of ethoxylation in the surfactant mixture and is varied by changing the weight ratio of ethoxylated surfactants. Listed under the column heading microemulsion (ME) type is the phase separation characteristic of a given composition. An upper phase microemulsion (U) forms at low H/L ratio and high salinity as a phase-separated system where an oil-continuous microemulsion is in equilibrium with excess settled water. A lower phase microemulsion (L) forms at high H/L ratio and low salinity as a system where water-continuous microemulsion is in equilibrium with excess floating oil. A single phase microemulsion (S) forms over a relatively narrow range of H/L ratios and salinity and is a relatively clear, thermodynamically stable dispersion containing all the components. The last column lists the nephelometer turbidity units (NTU), which are a measure of single phase microemulsion clarity. Below -50 NTU the system looks quite bright. From ~50 to 100 NTU the system is clear but with very slight haze developing. From 100 to 200

Example VI

Hydrogen Peroxide Diesel Fuel Microemulsions

Another approach to raising the cetane number of microemulsified fuels is the incorporation of aqueous hydrogen peroxide. The following table shows that direct replacement of water with 3% H₂O₂ in the salt-free microemulsion results in a clear, stable microemulsion without rebalancing.

Microemulsions in DF2 Containing Cetane Improvers

Surfactant, g/dl		Aqueous Phase	ME	
<u>C12XS-MEA</u>	<u>C12XS-E5</u>		<u>Type</u>	<u>NTU</u>
2.00	2.00	Water	S	68
2.00	2.00	3% H ₂ O ₂	S	55

All Systems Contain 10 Vol. % aqueous + 90 Vol. % DF2.

Example VII

Oleate Surfactants for Diesel Fuel Microemulsions

The advantage for carboxylate surfactants is that they do not add sulfur to the diesel fuel microemulsion composition. Sulfur-containing compounds in diesel fuel are environmentally undesirable since they may lead to sulfur oxides in the diesel exhaust. Some localities have established maximum sulfur levels in diesel fuels; California, for example, specifies no more than 500 ppm. The examples in Table IV show that oleate surfactants are effective in preparing single phase microemulsions of water and aqueous NH₄NO₃ in diesel fuel. The aqueous phase to surfactant ratio is 2.5:1 indicating that the instant ethoxylated alkyl ammonium oleate surfactants are efficient microemulsifiers when properly balanced. As in the case with the ethoxylated alkyl ammonium alkyl aryl sulfonates, increasing ethoxylation is required to balance the surfactants when using higher NH₄NO₃ concentrations. This shows the criticality of surfactant balancing which depends strongly on aqueous phase composition. Temperature sensitivity is again minimized by blending two or more surfactants with opposing temperature dependencies; MEA-oleate becomes more hydrophilic while the ethoxylated alkyl ammonium oleate become more lipophilic with increasing temperature. Blends of these surfactants give temperature insensitive microemulsions.

TABLE IV
Oleate Surfactant Stabilized Microemulsions¹⁾

MEA Oleate	Surfactant, g/dl				E18-13 Oleate	X NH ₄ NO ₃ ²⁾	ME Type
	E18-2 Oleate	E18-5 Oleate	E18-10 Oleate	E18-13 Oleate			
1.67	1.67	0.66	-	-	-	1	U
1.67	1.50	0.83	-	-	-	1	S
1.67	1.33	1.00	-	-	-	1	L
2.00	-	2.00	-	-	-	5	U
2.00	-	1.83	0.17	-	-	5	S
2.00	-	0.67	0.33	-	-	5	L
2.00	-	0.17	1.83	-	-	10	U
2.00	-	-	2.00	-	-	10	S
2.00	-	-	1.83	0.17	-	10	L
2.00	-	-	1.67	0.33	-	10	U
2.00	-	-	1.33	0.67	-	10	S
2.00	-	-	1.00	1.00	-	10	L

1) All systems contain 10 Vol. % aqueous and 90 Vol. % DF2.

2) Based on water content.

Claims

1. A fuel composition which comprises:
- a fuel;
 - about 1.0 to about 30.0 weight percent of water based upon said diesel fuel;
 - about 0 to about 30 weight percent of an alkanol based upon said water, said alkanol having about 1 to about 3 carbon atoms;
 - less than about 20.0 weight percent of an additive based upon said water, said additive being selected from the group consisting of an inorganic oxidizer, a polar organic oxidizer and a nitrogen oxide-containing compound; and
 - about 0.5 to about 15.0 weight percent of a surfactant system based on said diesel fuel, said surfactant system comprising a blend of a hydrophilic surfactant and a lipophilic surfactant in a ratio sufficient to form a single phase translucent microemulsion, wherein said diesel fuel exhibits improved cetane and combustion properties, reduced smoke, soot emissions, particulate emissions and NOx emissions in the combustion of said diesel fuel in a diesel engine.
2. A fuel composition according to claim 1, wherein the fuel is diesel, gasoline or jet fuel, preferably diesel fuel.
3. A fuel composition according to claim 1 or 2, wherein the hydrophilic and lipophilic blend of surfactants is comprised of two or more surfactants selected from one or more of:
- an alkali metal, ammonium, alkyl ammonium, alkanol ammonium, or ethoxylated alkyl or alkanol ammonium salt of an alkyl or alkylaryl sulfonic acid of the generic formula:
- $$\text{R-SO}_3\text{H}$$
- wherein R is an alkyl or alkyl benzene group containing 8 to 30 carbon atoms in the alkyl chain and the benzene ring may be additionally substituted with one or two alkyl groups containing 1-3 carbon atoms each;
- an ethoxylated surfactant of the generic formula:
- $$\text{R}_1\text{x}(\text{CH}_2\text{CH}_2\text{O})_n\text{Y}$$
- wherein R₁ is an alkyl or mono- or di-alkyl aryl group containing 8 to 30 carbon atoms,
- $$\begin{array}{ccccccc} \text{H} & \text{R}_2 & \text{R}_2 & & \text{O} & \text{O} & \text{O} \\ | & | & | & & || & || & || \\ \text{X is } -\text{O}- & -\text{S}- & -\text{N}- & -\text{H}- & [-\text{N}-] & ^+\text{Cl}^- & -\text{C}-\text{O}- & -\text{C}-\text{OR}_4\text{O}- & -\text{C}-\text{NH}- & \text{or} & -\text{SO}_2\text{NH}- \\ | & & & & & & & & & & \\ \text{R}_3 & & & & & & & & & & \end{array}$$
- and Y is -H-, -SO₃-M⁺ or -(PO₃H)-M⁺ wherein M⁺ is an inorganic or ammonium cation including alkyl substituted ammonium cations; R₂ is an alkyl group containing 1 to 20 carbon atoms or a polyethoxy ether group containing from 1 to 30 (CH₂CH₂O) groups; R₃ is H or an alkyl group containing 1 to 3 carbon atoms; R₄ is a polyhydroxy group derived from glycerol, glycols, sorbitol, or various sugars; and n is an integer of from 1 to 30; and
- an alkali metal, ammonium, alkyl ammonium, alkanol ammonium, or ethoxylated alkyl ammonium salt of an alkyl carboxylic acid of the generic formula
- $$\text{R}'-\text{COOH}$$
- wherein R' is an alkyl group of 8 to 24 carbon atoms.
4. The composition of claim 3 wherein at least one of the lipophilic surfactants is an ethoxylated C₁₂-C₁₈ alkyl ammonium salt of a C₈-C₂₄ alkyl carboxylic or alkylaryl sulfonic acid containing less than 6 ethylene oxide groups.
5. The composition of claim 3 or 4 wherein at least one of the hydrophilic surfactants is an ethoxylated C₁₂-C₁₈ alkyl ammonium salt of a C₈-C₂₄ alkyl carboxylic or alkylaryl sulfonic acid containing 6 or more ethylene

oxide groups.

6. A process for reducing smoke, soot emissions, particulate emissions, and NOx emissions in the combustion of a diesel fuel in a diesel engine which comprises the step of adding to said diesel fuel about 1.0 to about 30.0 weight percent of water and about 0.5 to about 15.0 weight percent of a surfactant system, based on said diesel fuel, said surfactant system comprising a blend of a hydrophilic surfactant and a lipophilic surfactant in a ratio sufficient to form a single phase translucent microemulsion, whereby smoke, soot, particulate and NOx emissions are reduced.
7. A process according to claim 6, wherein said hydrophilic surfactant is selected from the group consisting of alkali metal, ammonium, 1 to 3 carbon alkyl ammonium, 2 to 6 carbon alkanol ammonium containing 1 to 3 hydroxy groups, and 6 or more ethoxy C₁₂-C₁₈ alkyl ammonium salts of alkyl carboxylic acids and alkyl aryl sulfonic acids and 6 or more ethoxy alkyl phenols.
8. A process according to claim 6 or 7, wherein said lipophilic surfactant is selected from the group consisting of less than 6 ethoxy alkyl phenols and less than 6 ethoxy C₁₂-C₁₈ alkyl ammonium salts of alkyl carboxylic and alkyl aryl sulfonic acids.

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(54) Title: EMULSION BLENDS

(57) Abstract

Emulsion blends are provided containing Fischer-Tropsch hydrocarbons, non-Fischer-Tropsch hydrocarbons, water, and a surfactant.

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EMULSION BLENDS

FIELD OF THE INVENTION

This invention relates to emulsions comprising Fischer-Tropsch derived liquids and hydrocarbon liquids other than Fischer-Tropsch liquids, e.g., petroleum liquids, and water.

BACKGROUND OF THE INVENTION

Hydrocarbon in water emulsions are well known and have a variety of uses, e.g., as fuels for power plants or internal combustion engines. These emulsions are generally described as macro-emulsions, that is, where the emulsion is cloudy or opaque as compared to micro-emulsions that are essentially clear, translucent, and more thermodynamically stable than macro-emulsions, the micro-emulsions having a higher level of surfactant.

While aqueous fuel emulsions are known to reduce pollutants when burned as fuels, the methods for preparing emulsions and the materials used therein, e.g., surfactants and co-solvents, such as alcohols, can be expensive. Also, the thermodynamic stability of macro-emulsions is relatively weak, particularly when low levels of surfactants are used in preparing the emulsions.

Consequently, there is a need for stable macro-emulsions that employ less surfactants or co-solvents, and use less costly materials in preparing hydrocarbon in water emulsions. Additionally, by virtue of the invention described herein, distillate fuel emulsions of conventional petroleum fuels can be upgraded, for example, to higher cetane index, by blending with Fischer-Tropsch derived hydrocarbon liquids, e.g., distillates.

For purposes of this invention, the stability of macro-emulsions is determined generally as the degree of separation occurring during a twenty-four hour period, usually the first twenty-four hour period after forming the emulsions.

SUMMARY OF THE INVENTION

In accordance with this invention, a distillate emulsion is provided which comprises water, a Fischer-Tropsch hydrocarbon, a hydrocarbon other than a Fischer-Tropsch hydrocarbon, and a surfactant where the amount of surfactant employed is less than or equal to, preferably less than, the amount of surfactant required to emulsify either hydrocarbon by itself. Thus, a synergistic effect occurs when non-Fischer-Tropsch hydrocarbon distillates are emulsified with water in the presence of Fischer-Tropsch hydrocarbon distillates.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a plot of the minimum amount of surfactant required (ordinate) to emulsify blends of Fischer-Tropsch distillates and conventional petroleum distillates (abscissa).

PREFERRED EMBODIMENTS

By virtue of this invention, relatively stable, macro-emulsions are prepared in the substantial absence, e.g., ≤ 1.0 wt % or complete absence of the addition of a co-solvent, e.g., alcohols, and preferably in the substantial absence of co-solvent. Thus, Fischer-Tropsch liquids may contain trace amounts of oxygenates, including alcohols, these oxygenates being lower in concentration in the emulsions than would be present if an alcohol or other oxygen containing co-solvent was added to the emulsion. Generally, the alcohol content of the Fischer-Tropsch liquids is nil in the sense of not being

279

279

measurable, and is generally less than about 1 wt% based on the liquids, more preferably less than about 0.1 wt% based on the liquid.

The Fischer-Tropsch liquids used in this invention are those hydrocarbons that are liquid at room temperature. Thus, these materials may be the raw liquids from the Fischer-Tropsch hydrocarbon synthesis reactor, such as C_4+ liquids, preferably C_3+ liquids, more preferably $C_3 - C_{17}$ hydrocarbon containing liquids, or hydroisomerized Fischer-Tropsch liquids such as C_3+ liquids. These materials generally containing at least about 90 wt% paraffins, normal or isoparaffins, preferably at least about 95 wt% paraffins, and more preferably at least about 98 wt% paraffins.

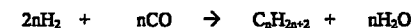
The Fischer-Tropsch hydrocarbons may be further characterized as fuels: for example, naphthas, e.g. boiling in the range C_4 to about 320°F , preferably $C_3 - 320^\circ\text{F}$, water emulsions of which may be used as power plant fuels; transportation fuels, jet fuels, e.g., boiling in the range of about $250 - 575^\circ\text{F}$, preferably $300 - 550^\circ\text{F}$, and diesel fuels, e.g., boiling in the range of about $320 - 700^\circ\text{F}$. Other liquids derived from Fischer-Tropsch materials and having higher boiling points are also included in the materials used in this invention.

The non-Fischer-Tropsch hydrocarbons can be obtained from a variety of sources, e.g., petroleum, shale liquids (kerogen), tar sand liquids (bitumen), or coal liquids. Preferred materials are petroleum derived hydrocarbons boiling in the same ranges as described for the Fischer-Tropsch hydrocarbon containing liquids.

Generally, the emulsions contain less than 100 wt% of either Fischer-Tropsch hydrocarbon containing liquids or non-Fischer-Tropsch hydrocarbons containing liquids. Preferably, however, the Fischer-Tropsch liquids are present in amounts of about 10-90 wt% of the total hydrocarbons, more preferably at least about 20 wt% Fischer-Tropsch liquids, still more preferably 25-75 wt%, and still more preferably 40-60 wt% Fischer-Tropsch liquids.

The amounts of water and totally hydrocarbons in the emulsions can also vary over a wide range, for example, 90/10 hydrocarbon/water to 10/90 hydrocarbon/ water. Preferably, however, the hydrocarbon content will be greater than about 50 wt%, preferably greater than about 60 wt%, more preferably 60-85 wt%.

While any kind of water may be used, the water obtained from the Fischer-Tropsch process, e.g.,



is particularly preferred, the process water from a non-shifting process.

A generic composition of Fischer-Tropsch process water, in which oxygenates are preferably ≤ 2.0 wt%, more preferably less than 1 wt% and useful for preparing hydrocarbon emulsions is shown below:

C_1 - C_{12} alcohols	0.05 -2 wt%, preferably 0.05 - 1.2 wt%
C_2 - C_6 acids	0-50 wppm
C_2 - C_6 Ketones, aldehydes	
acetates	0-50 wppm
other oxygenates	0-500 wppm

Fischer-Tropsch derived materials usually contain few unsaturates, e.g., ≤ 1 wt%, olefins and aromatics, preferably less than about 0.5 wt% total aromatics, and nil-sulfur and nitrogen, i.e., less than about 50 ppm by weight sulfur or nitrogen. Hydrotreated Fischer-Tropsch liquids may also be used which contain virtually zero or only trace amounts of oxygenates, olefins, aromatics, sulfur, and nitrogen.

The non-ionic surfactant is usually employed in amounts equal to or lower than that required for emulsifying petroleum derived liquids. Thus, the surfactant concentration used is sufficient to allow the formation of the macro, relatively stable

emulsion. Preferably, the amount of surfactant employed is at least about 0.001 wt% of the total emulsion, more preferably at least about 0.01 wt%, still more preferably about 0.05 to about 5 wt%, and still more preferably 0.05 to less than 3 wt%, and most preferably 0.05 to less than about 3 wt%, and most preferably 0.05 to less than about 2 wt%.

Typically, surfactants useful in preparing the emulsions of this invention are non-ionic and are non-ionic and are those used in preparing emulsions of petroleum derived or bitumen derived materials, and are well known to those skilled in the art. These surfactants usually have a HLB of about 7-25, preferably 9-15. Useful surfactants for this invention include ethoxylated alkylphenols with 5 - 30 moles of ethyleneoxide per molecule, linear alcohol ethoxylates, ethoxylated octylphenol, fatty alcohol ethoxylates, ethoxylated stearic acid, stearyl alcohol ethoxylates, ethoxylated dialkyl phenol, and alkyl glycosides, preferably ethoxylated alkyl phenols, and more preferably ethoxylated nonylphenols with about 8-15 ethylene oxide units per molecule. A particularly preferred emulsifier is an alkyl phenoxy polyalcohol, e.g., nonyl phenoxy poly (ethyleneoxy ethanol), commercially available from several sources, including the trade name Igepol.

The use of water-fuel emulsions significantly improves characteristics of the fuels and particularly so in respect of the materials of this invention where Fischer-Tropsch water emulsions have better emission characteristics than petroleum derived emulsions, i.e., in regard to particulate emissions and NO_x.

The emulsions of this invention are formed by conventional emulsion technology, that is, subjecting a mixture of the hydrocarbon, water and surfactant to sufficient shearing, as in a commercial blender or its equivalent for a period of time sufficient for forming the emulsions, e.g., generally a few seconds. For emulsion information, see generally, "Colloidal Systems and Interfaces", S. Ross and I. D. Morrison, J. W. Wiley, NY, 1988.

The Fischer-Tropsch process is well known in these skilled in the art, see for example, U.S. Patent Nos. 5,348,982 and 5,545,674 incorporated herein by reference and typically involves the reaction of hydrogen and carbon monoxide in a molar ratio of about 0.5/1 to 4/1, preferably 1.5/1 to 2.5/1, a temperatures of about 175-400°C, preferably about 180 - 240°C, a pressures of 1-100 bar, preferably about 10-50 bar, in the presence of a Fischer-Tropsch catalyst, generally a supported or unsupported Group VIII, non-noble metal, e.g., Fe, Ni, Ru, Co and with or without a promoter, e.g. ruthenium, rhenium, hafnium, zirconium, titanium. Supports, when used, can be refractory metal oxides such as Group IVB, i.e., titania, zirconia, or silica, alumina, or silica-alumina. A preferred catalyst comprises a non-shifting catalyst, e.g., cobalt or ruthenium, preferably cobalt, with rhenium or zirconium as a promoter, preferably cobalt/rhenium supported on alumina, silica or titania, preferably titania. The Fischer-Tropsch liquids, i.e., C₅+, preferably C₁₀+, are recovered and light gases, e.g., unreacted hydrogen and CO, C₁ to C₃ or C₄ and water are separated from the hydrocarbons.

Hydroisomerization conditions for Fischer-Tropsch derived hydrocarbons are well known to those skilled in the art. Generally, the conditions include:

CONDITION	BROAD	PREFERRED
Temperature, °F	300-900 (149 - 482°C)	550-750 (288-399°C)
Total pressure, psig	300-2500	300-1500
Hydrogen Treat Rate, SCF/B	500-5000	2000-4000

Hydrocarbon consumption is a result of conditions.

Catalysts useful in hydroisomerization are typically bifunctional in nature containing an acid function as well a hydrogenation component. A hydrocracking suppressant may also be added. The hydrocracking suppressant may be either a Group IB metal, e.g., preferably copper, in amounts of about 0.1-10 wt%, or a source of

sulfur, or both. The source of sulfur can be provided by presulfiding the catalyst by known methods, for example, by treatment with hydrogen sulfide until breakthrough occurs.

The hydrogenation component may be Group VIII metal, either noble or non-noble metal. The preferred non-noble metals can include nickel, cobalt, or iron, preferably nickel or cobalt, more preferably cobalt. The Group VIII metal is usually present in catalytically effective amounts, that is, ranging from 0.1 to 20 wt%. Preferably, a Group VI metal is incorporated into the catalyst, e.g., molybdenum, in amounts of about 1-20 wt%.

The acid functionality can be furnished by a support with which the catalytic metal or metals can be composited by well known methods. The support can be any refractory oxide or mixture of refractory oxides or zeolites or mixtures thereof. Preferred supports include silica, alumina, silica-alumina-phosphates, titania, zirconia, vanadia and other Group III, IV, V or VI oxides, as well as Y sieves, such as ultra stable Y sieves. Preferred supports include silica-alumina where the silica concentration of the bulk support is less than about 50 wt%, preferably less than about 35%, more preferably 15-30 wt%. When alumina is used as the support, small amounts of chlorine or fluorine may be incorporated into the support to provide the acid functionality.

A preferred support catalyst has surface areas in the range of about 180-440 m²/gm, preferably 230-350 m²/gm, a bulk density of about 0.5-1.0 g/ml, and a side crushing strength of about 0.8 to 3.5 kg/mm.

The preparation of preferred amorphous silica-alumina microspheres for use as supports is described in Ryland, Lloyd B., Tamele, M. W., and Wilson, J. N., *Cracking Catalysts, Catalysis*, Volume VII, Ed. Paul H. Emmett, Reinhold Publishing Corporation, New York, 1960.

During hydroisomerization, the 700°F+ conversion to 700°F-ranges from about 20-80%, preferably 30-70%, more preferably about 40-60%, and essentially all olefins and oxygenated products are hydrogenated.

The catalysts can be prepared by any well known method, e.g., impregnation with an aqueous salt, incipient wetness technique, followed by drying at about 125-150°C for 1-24 hours, calcination at about 300-500°C for about 1-6 hours, reduction by treatment with a hydrogen or a hydrogen containing gas, and, if desired, sulfiding by treatment with a sulfur containing gas, e.g., H₂S at elevated temperatures. The catalysts will then have about 0.01 to 10 wt% sulfur. The metals can be composited or added to the catalyst either serially, in any order, or by co-impregnation of two or more metals.

To exemplify this invention several emulsions blends were prepared at room temperature, although preparation temperatures may range from about 10-100°C, preferably 15-30°C.

The surfactant was first mixed with water and blended in a Waring blender for 5 seconds. Then the hydrocarbon was added and blended for one (1) minute. If an emulsion did not form, blending was continued in one (1) minute sequences, checking for an emulsion after each minute. If an emulsion did not form after a total of five (5) minutes blending time, emulsification was not successful.

We used the following conditions:

Surfactant: Igepol CO-630 (Rhône-Poulenc); ethoxylated nonylphenol with 9 moles EO

Water: Hydrocarbon ratio: 30/70

Blend amount: 200 ml

Water type: tap water

Hydrocarbons: Fischer-Tropsch diesel (250-700° F boiling range) described below and a conventional, petroleum derived European summer grade diesel fuel. The Fischer-Tropsch diesel was prepared by converting hydrogen and carbon monoxide ($H_2:CO$ 2.11-2.16) to heavy paraffins in a slurry Fischer-Tropsch reactor with a titania supported cobalt/rhenium catalyst described in U.S. Patent No. 4,568,663. The reaction conditions were about 425°F and 288 psig and a linear gas velocity of 17.5 cm/sec. The alpha was 0.92. The Fischer-Tropsch wax which was predominantly 500°F+ was hydroisomerized in a flow through fixed bed unit using a cobalt and molybdenum amorphous silica-alumina catalyst as described in U.S. 5,292,989 and U.S. 5,378,348. Hydroisomerization conditions included 708°F, 750 psig H_2 2500 SCF/B H_2 and a liquid hourly space velocity (LHSV) of 0.7 - 0.8. Hydroisomerization was conducted with recycle of 700°F reactor wax. The combined feed ratio (Fresh Feed + Recycle Feed)/Fresh Feed was 1:5. The product was then fractionated and a nominal 320-700°F cut diesel was recovered. This product contained nil sulfur, nitrogen, aromatics, oxygen (ates), and unsaturates and is essentially 100% paraffinic.

Eleven tests were prepared with Tests 1 and 11 being 100% petroleum derived diesel and 100% Fischer-Tropsch derived diesel, respectively, shown in Table I below.

Table I

Test #	Petroleum Derived Diesel	Fischer-Tropsch Diesel	Surfactant
1	0	100	0.3
2	25	75	0.25
3	25	75	0.3
4	40	60	0.2
5	50	50	0.15
6	50	50	0.1
7	60	40	0.3
8	75	25	0.35
9	75	25	0.3
10	90	10	0.3
11	100	0	0.75

This data is plotted and shown graphically in Figure 1. From the graph, it is clear that the minimum surfactant concentration for emulsifying 100% petroleum derived diesel was 0.75 wt%, while the minimum surfactant required for emulsifying 100% Fischer-Tropsch hydrocarbons was 0.3%. The table and Figure 1 show clearly that no more than 0.3 wt% surfactant was required to emulsify any combination of petroleum derived and Fischer-Tropsch derived hydrocarbons. Nevertheless, for the surfactant required to emulsify either hydrocarbon, we could expect the required amount of surfactant to emulsify any mixture of the two hydrocarbons to fall on or around the dotted line.

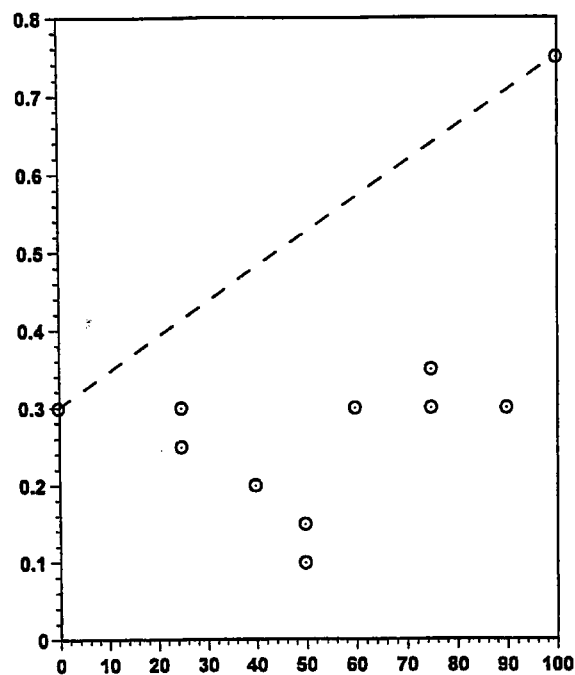


FIG. 1

INTERNATIONAL SEARCH REPORT

 (Int. J. Appl. No.)
 PCT/US 98/18997

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C10L1/32

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

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C10L

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 209 758 A (HUELS CHEMISCHE WERKE AG) 28 January 1987	
A	EP 0 363 300 A (OCCIDENTAL PETROLEUM CANADA) 11 April 1990	
A	US 5 545 674 A (MAULDIN CHARLES H ET AL) 13 August 1996 cited in the application	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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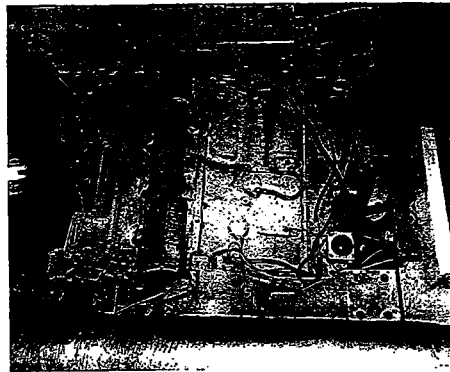
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(64) Title: **AN ADDITIVE COMPOSITION ALSO USED AS A FUEL COMPOSITION COMPRISING WATER SOLUBLE ALCOHOLS**

(57) Abstract

The present invention relates to an additive composition for a combustible fuel to produce improved combustion and reduced smoke and particulates production of the combusted fuel, which additive composition comprises: a) one or more water-soluble alcohols selected from the group consisting of alcohols having from between 1 and 5 carbon atoms, in an anhydrous state or as a 0.5-36 % aqueous solution, and optional one or more of the following: b) one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between 6 and 18 carbon atoms; c) one or more alcohols selected from the group consisting of ethoxylated, straight- or branched-chain alcohols having between 12 and 18 carbon atoms, wherein the ethylene oxide add-on is less than 5 moles; d) a fatty acid of the structure R-(C=O)-OH, wherein R is selected from alkyl, alkenyl or alkynyl having from 10 to 24 carbon atoms, with e) a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of urea, guanidine, alkyl hydrazine, dialkyl hydrazine, urea, guanidine, monomethyl ethanolamine, dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded; wherein component a) to e) when combined with mixing with said combustible fuel form a clear stable microemulsion having a viscosity similar to a liquid fossil fuel; and wherein said additive composition excludes glycine, polyethylene, compounds, metals, metal compounds, compounds of phenanthrene, sulfur, sulfur compounds, polyoxypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene.



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AN ADDITIVE COMPOSITION ALSO USED AS A FUEL COMPOSITION
COMPRISING WATER SOLUBLE ALCOHOLS

BACKGROUND OF THE INVENTION

5 Related Applications

This application is a continuation-in-part application of U.S. Serial No. 60/071,181, filed January 12, 1998; U.S. Serial No. 60/079,686, filed March 27, 1998; and U.S. Serial No. 60/093,305, filed July 17, 1998, all of which are incorporated herein by reference in their entirety.

10 Field of the Invention

The present invention concerns a novel composition of ingredients which are used as an additive to a combustible liquid fuel to produce a clear stable solutions or microemulsions with the fuel. The additive meets or exceeds liquid property specification requirements of the combustible fuel and greatly improves the overall
15 combustion of the fuel while reducing significantly unwanted smoke, particulates, toxic gases, noxious gases and the like. Specifically the additive composition includes one or more of the following: aqueous or anhydrous water-soluble alcohols and includes optionally one or more of the following: water-insoluble alcohols; ethoxylated alcohols; and fatty acids partially neutralized with a volatile source of basic nitrogen,
20 while specifically limiting the use of ethylene oxides and specifically excluding conventionally used glycerine, esterification products, metals, non-biodegradable solvents, and certain other components.

Description of Related Art

Much research, effort and time have been expended to produce fuel
25 compositions for internal combustion engines which show significant decreases upon combustion of toxic exhaust gases or vapors, particulates, smoke, and the like without sacrifice of engine performance or efficiency.

It is currently known by those skilled in the art that the introduction of oxygenators into fossil fuels contributes to better burning and the reduction of toxic
30 exhaust emissions. Ethanol is one such oxygenator which, when used with gasoline for instance, reduces toxic emissions.

A problem, however, is that ethanol attracts water and will separate from gasoline in the presence of certain amounts of water condensation. Another problem is

that ethanol is generally denatured using methanol, which exacerbates the problem of water separation and produces unacceptable solvency levels, such that ethanol/methanol/gasoline mixtures cannot be transported through existing pipelines.

The present invention solves the problem of water condensation in the presence of
5 ethanol/gasoline mixtures by creating clear microemulsions that are bio-degradeable, do not separate, and actually make use of small amounts of water for superior combustion temperatures. The present invention also solves the problem of solvency levels of ethanol/gasoline mixtures by utilizing components that meet storage and shipping requirements for gasoline.

10 Another problem associated with using ethanol as an oxygenator is that ethanol, as well as methanol and other water-soluble alcohols, will not mix at all with less refined fossil fuels, such as Diesel fuel or other distillate fuels like kerosene.

The present invention makes it possible to introduce ethanol into Diesel and other distillate fuels, forming bio-degradable clear, stable solutions and microemulsions
15 that will absorb water condensation for optimal combustion temperatures and uses other water-soluble alcohols for their oxygenating properties.

There are many components which when mixed together form emulsions with liquid hydrocarbons, fuels, refined renewable resources (vegetable oils) and the like. However, most mixtures of components do not meet the present set of fuel storage and
20 combustion regulations and engine performance parameters.

These requirements include, for example:

A fuel/additive composition must form a clear, stable, water-in-oil microemulsion where water and water-soluble components are very finely dispersed throughout the continuous phase which must be the oil phase.

25 In order for efficient combustion to occur, the flame front in the combustion chamber must contact oil first to maintain optimum combustion temperature. The presence of any water at all will reduce combustion temperature. The presence of an optimal amount of water and water-soluble alcohol inside the oil droplet (in the micelle of the micro-emulsion) produces balanced, optimal fuel/oxygen ratios and combustion
30 temperatures where carbon present is more completely burned.

When this slightly reduced but still high level of heat reaches the extremely fine water droplet, the water is transformed into steam. The expansion of liquid water to steam (at a ratio of 1:600) also produces power of its own, which further enhances

engine performance.

On the other hand, an oil-in-water emulsion will not perform in the same way. With water as the continuous phase, water contacts the flame front first. The water diminishes or puts the fire out, and then the smoldering flame contacts oil. The results of this incomplete combustion are extremely high hydrocarbon (unburned fuel), particulates, smoke, etc. emissions and significantly reduced power. Nitrogen oxides are usually reduced; however, that is because the temperature of combustion is also reduced below any efficiency level.

Diesel engines are particularly suited to fuel/additive combustion enhancement.

Compression ignition engines rely on the heat of compression to produce combustion of fuel; however, it is the compression and expansion of air that is the important power dynamic which makes Diesel engines highly effective.

Fuel/additive power enhancement works on the same principle. At the top of the compression stroke, a small amount of fuel/alcohol/water mixture ignites and explodes. The fuel burns, and now both air and steam expand together to produce power.

Fuel/additive combustion enhancement is made possible by the presence of increased oxygen levels provided by water-soluble alcohols and water. An optimal fuel:oxygen ratio is produced allowing for the complete combustion of available carbon.

The same principle works in a gasoline, spark-ignited engine. As spark-ignited engines are designed, power comes only from the expansion of the explosion of gasoline which is limited compared to the power produced by the compression and expansion of air. The fuel/additive gives these relatively low-efficiency engines the benefit of the water to steam expansion as well as improved oxygenation for more complete burning of carbon.

Even though they produce much greater power levels, the emissions problem associated with Diesel engines has always been difficult to solve. Diesel fuel is usually too rich in hydrocarbons to maintain the delicate balance required for optimal power and complete burning of carbon. Without modification, Diesel fuel burns incompletely. Diesel fuel contains too much carbon in relation to the amount of available oxygen and for what it has to accomplish in the split second before the piston starts moving away from its highest compression (heat) point.

The addition of certain oils, alcohols, and water produce an efficient combination and combustion is extremely enhanced. Vegetable-based components and most alcohols have slightly lower cetane (BTU) value than other fuels. However, water and water-soluble alcohols increase available oxygen and maintain optimal temperatures in the combustion chamber so that essentially all available carbon is burned and utilized for power, rather than being emitted as carbon particles in exhaust smoke. At the same time, water enhances power through expansion as steam and cleans engine parts with its detergent properties.

Although some of the following components may be useful in producing clear, stable microemulsions, they cannot be included in a formulation intended for use as a fuel in an internal combustion engine.

The U.S. Environmental Protection Agency (EPA) specifically rules against fuel compositions with sulphur, aromatic hydrocarbons, and metals of any kind because of the resulting detrimental emissions byproducts. To meet EPA and California (CA) Air Resources Board (CARB) standards only the elements carbon, hydrogen, oxygen, or nitrogen (CHON) can be included.

For instance, sodium or potassium salts in the presence of fatty acids also form a microemulsion, but do not fall into the CHON classification, and also cannot be used because of excessive corrosive properties.

Even among possible components that fall within the CHON classification, many are still unsuitable for the intended use. For example, ethylene oxides enhance microemulsion stability, but impede combustion, and can be used only in very limited amounts.

Even among possible CHON components that show promising combustion qualities, many are still unsuitable for optimum performance. For an additive composition to be useful it must meet these qualifications:

1. It must be stable at high and low temperatures.
2. It must maintain a viscosity similar to fossil fuel in all temperature and pressure conditions.
3. It must not damage engine or fuel system parts.
4. It must be usable with little or no retrofit of engine or fuel system parts.
5. It must maintain a power level suitable to its particular application.
6. It must show an improvement in engine performance or emissions and

preferably both.

7. It must not increase nitrogen oxides or hydrocarbon or carbon monoxide emissions.

Methyl esters are often used as a fossil fuel additive; however, glycerides must be removed during the esterification process, reducing and even eliminating, cost effectiveness. Gelling problems hamper their use, especially at low temperatures, and typically, methyl esters have been producing about a 5% increase in nitrogen oxides in older engines, making them unusable as far as the EPA and its regulations is concerned.

Another fuel additive is a water emulsion using naphtha as its base fuel. The purpose is to reduce NOx emissions. The composition uses as much as 40-50% water. Not only does an extra fuel tank need to be installed to carry the added liquid, hydrocarbon emissions (incomplete combustion) increase dramatically as the combustion flame front hits water. NOx emissions are also reduced, but that is because there is essentially insufficient combustion to cause a nitrogen/oxygen reaction.

Another fuel additive is methyltetrahydrofuran which is currently under study as a possible additive to introduce ethanol into Diesel fuel. However, methyl-tetrahydrofuran is a highly aggressive solvent known to attack and dissolve various metals, creating a high probability for damage to engine parts if used as a fuel in existing engines.

Another fuel additive is methyl tertiary butyl ether (MTBE) which successfully improves combustion characteristics of gasoline. However, MTBE is currently under investigation by the EPA, having been shown to be a toxic groundwater contaminant. As a result, its use is banned in several states.

Some prior research in the field includes, but is not limited to:

E. Wenzel et al. in U.S. Patent 3,608,530 and 5,025,759 disclose a compression ignition (Diesel) engine having paired opposed cylinders and a lever system interconnecting the pistons of the opposed power cycle cylinders with each other and with a crank shaft. Together, the long-stroke opposed-cylinders and smooth rotary type connection to the crankshaft produce optimal combustion efficiency and optimally balanced mechanical efficiency. However, even in this efficiently designed engine, standard Diesel fuel will produce unacceptable levels of emissions and by-products under current and planned EPA regulations. On the other hand, the present invention described herein below discloses a stable fuel composition for reducing Diesel fuel

emissions as well as incorporating components derived from renewable resources to augment dwindling fossil fuel supplies.

E. Wenzel et al. in U.S. Patent 4,083,698 disclose a clear stable liquid fuel composition for internal combustion engines. The fuel composition comprises a water-in-oil (w/o) emulsion of (a) a hydrocarbon fuel, (b) water, (c) a water-soluble alcohol and a combination of surface active agents, which are stable emulsions over a wide range of temperatures. However, in all described aspects, a non-ionic surfactant is a necessary component of the additive. In all described aspects this non-ionic surfactant includes an ethylene, polyethylene, polyoxyethylene and/or polyoxypropylene addition product.

A. W. Schwab et al. in U.S. Patent 4,451,267 disclose microemulsions for vegetable oil and aqueous alcohol with a trialkylamines surfactant as an alternative fuel for Diesel engines.

A. W. Schwab et al. in U.S. Patent 4,526, 586 disclose microemulsions from vegetable oil and aqueous alcohols with 1-butanol and optionally trialkylamines as an alternative fuel for Diesel engines. There is no disclosure in U.S. Patent 4,451,267 or 4,526,586 in which the vegetable oil emulsion is mixed with hydrocarbon fuels to form a water in oil (w/o) microemulsion with a hydrocarbon fuel.

W. Fridreich et al. in U.S. Patent 4,732,576 disclose a motor fuel and fuel oil emulsions using an organic salt as an emulsifier. Specific amine polyether diacid salts are a necessary component of the additive.

J.W. Foresberg et al. in U.S. Patent 5,360,458 disclose water-oil emulsions comprising water, oil, and a minor emulsifying amount of the reaction product of at least one saturated or unsaturated aliphatic monocarboxylic acid of about 12 to 24 carbon atoms. In all aspects, at least one acid of the general formula C_nH_nCOOH wherein n is between about 27 and 31 and having a phenanthrene nucleus and at least one amine are present as necessary components. In all aspects an aromatic hydrocarbon is a necessary component of the additive.

S.G. Schon et al. in U.S. Patent 5,004,479 disclose stable microemulsion fuel compositions which comprise (a) a hydrocarbon fuel such as Diesel fuel, jet fuel, gasoline, fuel oil, etc.; (b) water; and (c) a cosurfactant combination of methanol and a fatty acid which is partially neutralized by a nitrogenous base. In all aspects of U.S. Patent 5,004,479, methanol is the only alcohol present. Some U.S. Patents of

general background interest include:

4,406,519 and 4,451,265.

Other references of general background interest include:

J.J. Donnelly, Jr. and H.M. White, "Water and Alcohol Use in Automotive

5 Diesel Engines" DOE/DX/50286-4 published September 1985.

A.L. Compere et al., "Microemulsion Fuels: Development and Use" ORNL
TM-9603, published March 1985.

W.D. Weatherford, Jr. et al., AFLRL Reports 111, 13, 145, U.S. Army Fuels
and Lubricants Research Laboratory.

10 None of these patents, references, or articles teach or suggest the present
invention.

All patents, patent applications, articles, references, standards, etc. cited herein
are incorporated by reference in their entirety.

In spite of the present state of the art, a need still exists for improved

15 fuel/additive compositions which:

1. do improve combustion and reduce or eliminate smoke, particulates and
noxious gases;

2. do not damage engine or fuel system parts;

3. are usable with little or no retrofit of engine or fuel system parts;

20 4. are usable in varying proportions according to the requirements of
various applications;

5. meet federal EPA and state Air Resources Board standards; and

6. make use of renewable and readily available resources to partially or
fully replace fossil-based fuels.

25 The present invention provides such a range of improved compositions.

SUMMARY OF THE INVENTION

The present invention relates to an additive composition for a combustible fuel,
which is also used as a fuel composition, to utilize readily available and renewable
resources, to improve liquid combustible fuel properties, reduce undesirable elements such
30 as sulphur, aromatic hydrocarbons, and glycerine from the content of the fuel, produce
improved combustion, and to reduce visible smoke, particulates and other noxious
emissions production of the combusted fuel, which additive or fuel composition comprises:

a. one or more alcohols selected from the group consisting of water-soluble alcohols:

(i) having between about 1 and 2 carbon atoms, selected from the group
consisting of methanol and ethanol in an anhydrous state or as a 0.5-36% aqueous
solution by volume,

(ii) having between about 3 and 5 carbon atoms, selected from the group
5 consisting of propanol, iso-propanol, butanol, and pentanol by volume or combinations of
(a)(i) and (a)(ii); and

optionally one or more of the following:

b. one or more alcohols selected from the group consisting of:

(i) straight or branched chain, saturated or unsaturated alcohols, which are clear
10 and liquid at room temperature, and having between about 6 and 12 carbon atoms, or

(ii) straight- or branched-chain, saturated or unsaturated long-chain fatty
alcohols, which are solid at room temperature, having from between about 13 and 18
carbon atoms, or combinations of b(i) and (b)(ii);

c. one or more ethoxylated alcohols selected from the group consisting of
15 alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less
than 5 moles (units);

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl,
alkenyl or alkynyl having between about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected
20 from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine,
urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is
independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines
are excluded;

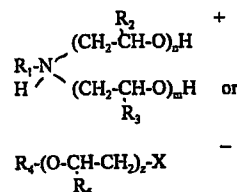
wherein components a and one or more of b, c, d, and e, when combined with
25 mixing with combustible fuel form a clear, stable microemulsion having a viscosity similar
to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive
ranges from about 99:1 to 0:100 by volume;

wherein said additive/fuel composition excludes ethylene glycol, glycerine,
polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds,
30 metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general
formula:

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10 wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 carbon atoms (e.g., alkyl or alkenyl) or R_4 is alkylphenyl of 1 to 18 carbon atoms in the optionally branched alkyl chain or H; R_2 , R_3 and R_5 each independently represent a methyl group or H, n plus m is an integer from 1 to 20; z is an integer from 0 to 15; and X is $-\text{COO}(-)$ or $-\text{OCH}_2\text{COO}(-)$,
 15 wherein, substituents R_2 , R_3 and R_5 are the same or different in different monomer units of each chain, and optionally other organic diacids are excluded.

In another aspect, the present invention relates to an additive composition for a refined combustible fuel, such as gasoline, to utilize readily available and renewable resources, improve liquid fuel properties, and produce improved fuel performance and
 20 combustion, which additive/fuel comprises a composition, which additive/fuel comprises a composition of components:

- a) one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 2 carbon atoms as defined herein in (a)(i) in an anhydrous state or as a 0.5-5% aqueous solution;
- 25 b) one or more alcohols selected from the group consisting of water-soluble alcohols having between about 3 and 5 carbon atoms as defined herein in (a)(ii)

wherein components a and b, are present in a:b ratios from about 80:20 and 99:1, wherein components a and b, when combined with mixing with the refined combustible
 30 fuel, such as gasoline, form a clear stable solution or microemulsion having a viscosity similar to that of the liquid fossil fuel and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99.

In another aspect, the present invention relates to an additive composition for a refined combustible fuel, such as gasoline, to utilize readily available and renewable
 35 resources, improve liquid fuel properties, and produce improved fuel performance and

10

combustion, which additive/fuel comprises a composition, which additive/fuel comprises a composition of components:

- a) one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 2 carbon atoms as defined herein in a(i) in an anhydrous state or as a 0.5-5% aqueous solution; and preferably a 0.5-1% aqueous ethanol;
- 5 b) one or more alcohols selected from the group consisting of water-soluble alcohols having between about 3 and 5 carbon atoms as defined herein in (a)(ii); and preferably iso-propanol:

10 wherein components a and b, are present in a:b ratios from about 80:20 and 99:1, and more preferably in a:b ratios range from 90:10 and 95:5 by volume wherein components a and b, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 and more
 15 preferably between about 80:20 and 99:1, and more preferably between about 90:10 and 95:5 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of
 20 components:

- a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution;
- b. one or more alcohols selected from the group consisting of clear, liquid
 25 saturated or unsaturated, straight- or branched-chain, alcohols having between about 6 and 12 carbon atoms,

wherein components a and b, are present in a:b ratios ranging from about 3:1 and 1:3, wherein components a and b, when combined with mixing with combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible
 30 fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 by volume.

In another aspect, the present invention relates to an additive composition for a

combustible fuel to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble
5 alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution; more preferably an anhydrous or about 5% aqueous ethanol denatured with methanol and most preferably an anhydrous or about 5% aqueous ethanol denatured with iso-propanol, butanol or combinations thereof;

b. one or more alcohols selected from the group consisting of saturated or
10 unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, more preferably between about 6 and 12 carbon atoms, and most preferably between about 8 and 10 carbon atoms; and

wherein components a and b, are present in a:b ratios ranging from about 3:1 by volume and 1:3, and more preferably in a:b ratios ranging from 3:1 and 1:1 by volume
15 wherein components a and b, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 and more preferably between about 80:20 and 99:1 and more preferably between about 90:10 and 95:5 by volume.

20 In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble
25 alcohols having between about 1 and 5 carbon atoms as defined herein, in an anhydrous state or as a 0.5-20% aqueous solution; and

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 12 carbon atoms; and

30 c. one or more alcohols selected from the group consisting of ethoxylated alcohols having between about 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

wherein components a, b, and c are present in a:b:c ratios ranging from about 4:1:1

and 1:4:4 by volume, wherein components a, b, and c when combined with mixing with the combustible fuel, form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 by volume.

5 In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble
10 alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution; more preferably an anhydrous or 5-10% aqueous ethanol denatured with methanol and most preferably an anhydrous or 5-10% aqueous ethanol denatured with iso-propanol, butanol or combinations thereof;

b. one or more alcohols selected from the group consisting of saturated or
15 unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, more preferably between about 6 and 12 carbon atoms, and most preferably between about 8 and 10 carbon atoms; and

c. one or more alcohols selected from the group consisting of ethoxylated alcohols having between about 6 and 18 carbon atoms, preferably between about 12 and
20 16 carbon atoms, where the ethylene oxide add-on is less than 5 moles and preferably 3 moles;

wherein components a, b, and c are present in a:b:c ratios ranging from about 4:1:1 and 1:4:4 by volume, and more preferably between about 4:1:1 and 4:2:1 by volume wherein components a, b, and c when combined with mixing with combustible fuel, form
25 a clear, stable microemulsion having a viscosity similar to that of the liquid fossil fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 and more preferably between about 80:20 and 99:1, and most preferably between about 90:10 and 95:5 by volume.

30 In another aspect, the present invention relates to an additive composition for a combustible fuel to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble

alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5 to 20% aqueous solution; and

b. one or more alcohols selected from the group consisting of ethoxylated alcohols having between about 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

wherein components a and b are present in a:b ratios ranging from between 3:1 and 1:2 by volume, wherein components a and b when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution; more preferably an anhydrous or 5-10% aqueous ethanol denatured with methanol and most preferably an anhydrous or 5-10% aqueous ethanol denatured with iso-propanol butanol or combinations thereof;

b. one or more alcohols selected from the group consisting of ethoxylated alcohols having between about 6 and 18 carbon atoms, preferably between about 12 and 16 carbon atoms, where the ethylene oxide add-on is less than 5 moles and preferably 3 moles;

wherein components a and b are present in a:b ratios ranging from 3:1 and 1:2 by volume, and more preferably between about 3:1 and 2:1 by volume, wherein components a and b when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99, and more preferably between about 80:20 and 99:1 and more preferably between about 90:10 and 95:5 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive/fuel comprises a composition of

components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms, such as mentanol, ethanol, propanol, iso-propanol, butanol, pentanol, in an anhydrous state or as a 0.5-36% aqueous solution;

and

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight-or-branched-chain alcohols having from between about 6 and 18 carbon atoms; and

c. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms; and

d. a source of nitrogen in an anhydrous state or as a aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded;

wherein components a, b and c are present in a:b:c ratios ranging from about 4:1:1 and 1:4:4; wherein components a, b, c, and d when combined with mixing with said combustible fuel form a clear, stable microemulsion having a viscosity similar to a liquid fossil fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution; more preferably an anhydrous or 5 to 10% aqueous ethanol denatured with methanol and most preferably an anhydrous or 5 to 10% aqueous ethanol denatured with isopropanol, butanol or combinations thereof;

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, more preferably between about 6 and 12 carbon atoms, and most preferably between about 8 and 10 carbon atoms;

c. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl,

alkenyl or alkynyl having from about 10 to 24 carbon atoms; and preferably saturated fatty acids, such as oleic acid and linoleic acid;

d. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or iso-propyl, wherein trialkylamines are excluded; sufficient to neutralize between about 40 to 85 percent of the fatty acid of subpart c;

wherein components a, b, and c are present in a:b:c ratios ranging from about 4:1:1 and 1:4:4; and preferably between about 4:1:1 and 4:2:1 by volume, wherein components a, b, c and d when combined with mixing with said combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99, and more preferably between about 80:20 and 99:1 and most preferably between about 90:10 and 95:5 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and

b. one or more alcohols selected from the group consisting of ethoxylated alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles; and

c. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms; and

d. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded,

wherein components a, b, and c are present in a:b:c ratios ranging from about 5:1:1

and 1:4:4 by volume; wherein components a, b, c, and d when combined with mixing with the combustible fuel, form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution; more preferably an anhydrous or 5 to 10% aqueous ethanol denatured with methanol and most preferably an anhydrous or 5 to 10% aqueous ethanol denatured with iso-propanol, butanol or combinations thereof;

b. one or more alcohols selected from the group consisting of ethoxylated alcohols having between about 6 and 18 carbon atoms, preferably between about 12 and 16 carbon atoms, where the ethylene oxide add-on is less than 5 moles and preferably 3 moles;

c. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, and preferably oleic acid or linoleic acid;

d. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded, sufficient to neutralize between about 40 to 85 percent of the fatty acid of subpart c;

wherein components a, b, and c are present in a:b:c ratios ranging from about 4:1:1 and 1:4:4; and preferably between about 4:1:1 and 3:1:1 by volume, wherein components a, b, c, and d when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99, and more preferably between about 80:20 and 99:1 and most preferably between about 90:10 and 95:5 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

- 5 a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and
 - b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 10 6 and 12 carbon atoms; and
 - c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles; and
 - d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, 15 alkenyl or alkynyl having from about 10 to 24 carbon atoms; and
 - e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine, wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines 20 are excluded;
- wherein components a, b, c, and d are present in a:b:c:d ratios ranging from about 6:1:1:1 and 1:4:4:4 by volume; wherein components a, b, c, d, and e when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: 25 additive ranges from about 99:1 to 1:99 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

- 30 a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution; more preferably an anhydrous or 5 to 10% aqueous ethanol denatured with methanol and most preferably an anhydrous or 5 to 10% aqueous

ethanol denatured with iso-propanol, butanol or combinations thereof;

- b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, more preferably between about 6 and 12 carbon atoms, and most preferably 5 between about 8 and 10 carbon atoms; and
 - c. one or more alcohols selected from the group consisting of ethoxylated alcohols having between about 6 and 18 carbon atoms, preferably between about 12 and 16 carbon atoms, where the ethylene oxide add-on is less than 5 moles and preferably 3 moles;
 - d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, 10 alkenyl or alkynyl having from about 10 to 24 carbon atom; and preferably oleic acid and linoleic acid;
 - e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, 15 urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded, sufficient to neutralize between about 40 to 85 percent of the fatty acid of subpart c;
- wherein components a, b, c, and d are present in a:b:c:d ratios ranging from about 20 6:1:1:1 and 1:4:4:4; and preferably between about 6:1:1:1 and 6:3:1:1 by volume, wherein components a, b, c, d, and e when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel:additive ranges from about 99:1 to 1:99, and more preferably between about 80:20 and 99:1 and more preferably between about 90:10 25 and 95:5 by volume.

Additional embodiments are found below in the DETAILED DESCRIPTION OF THE INVENTION.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1-6 show visible emissions from exhaust stacks as Stockton East Water 30 District, Stockton, CA.

Figure 1 is a photographic representation of the Caterpillar engine used at Stockton East Water District, Stockton, CA.

Figure 2 is a photograph of the containers of the additive blends.

Figure 3 is a photograph of the normal emissions of a diesel engine in start-up mode using CA#2 Diesel fuel.

Figure 4 is a photograph of the emissions of a diesel engine in start-up mode using the fuel additive blend of Example 1.

Figure 5 is a photograph of the emissions of a diesel engine normal running speed, using CA#2 Diesel fuel after 30 minutes or more.

Figure 6 is a photograph of the emissions of a diesel engine (far right smoke stack), normal running speed, using the fuel additive blend of Example 1.

Figures 7-18 show test procedure and 1-minute filter samples showing particulate reductions at Stockton East Water District.

Figure 7 is a photograph of the muffler and exhaust pipe from the diesel engine in Figure 1C, engine start-up mode using CA#2 diesel, showing method for collecting filter samples.

Figure 8 is a photograph of the muffler and exhaust pipe from the diesel engine in Figure 1, engine start-up mode using the fuel additive blend of Example 2 showing method for collecting filter samples.

Figure 9 is a photograph of the muffler and exhaust pipe from the diesel engine in Figure 1C, engine running mode, using the fuel additive blend of Example 2.

Figure 10 is a photograph of the muffler and exhaust pipe from the diesel engine in Figure 1, engine running mode, using the fuel additive blend of Example 2.

Figure 11 is a photograph showing on the left the filter sample 110A for engine running mode using CA#2 Diesel, and on the right of the photograph is the filter sample 110B after 10 min engine-running mode using the fuel additive blend of Example 2.

Figure 12 is a photograph showing on the left the filter sample 120A for engine running mode using CA#2 Diesel and on the right is the filter sample 120B after 30 min engine-running mode using the fuel additive blend of Example 2.

Figure 13 is a photograph showing on the left the filter sample 130A for engine running mode using CA#2 diesel and on the right is the filter sample 130B after 1 hr engine running mode using the fuel additive blend of Example 2.

Figure 14 is a photograph showing on the left the filter sample 140A for engine running mode using CA#2 Diesel and on the right the filter sample 140B after 10 min

engine-running mode using CA#2 Diesel, after 1hr use of the fuel additive blend of Example 2.

Figure 15 is a photograph showing on the left the filter sample 150A for engine startup mode using CA#2 Diesel and on the right the filter sample 150B for engine start-up mode using the fuel additive blend of Example 1 after 10 min use of the fuel additive blend.

Figure 16 is a photograph showing on the left the filter sample 160A for engine startup mode using CA#2, and on the right the filter sample 160B for engine start-up mode using the fuel additive blend of Example 1 after 1 hr use of the fuel additive blend.

Figure 17 is a photograph showing on the left the filter sample 170A for engine startup mode using CA#2 Diesel and on the right the filter sample 170B for engine start-up mode using CA#2 Diesel - after 1 hr use of the fuel additive blend.

Figure 18 is a photograph showing a comparison of all filter samples wherein filter sample 110A (is the same as 120A and 140A) as compared with 110B, 120B, and 140B, and filter sample 150A (is the same as 160A and 170A) as compared to 150B, 160B and 170B

Figure 19 is a photograph showing a comparison of filter samples from Example 4 wherein:

190A shows particulates from Test Cycle 1, Standard CA #2 Diesel fuel;
190B shows particulates from Test Cycle 2, Fuel/Additive Composition #1;
190C shows particulates from Test Cycle 3, Fuel/Additive Composition #2;
190D shows particulates from Test Cycle 4, Fuel/Additive Composition #3;
190E shows particulates from Test Cycle 5, Fuel/Additive Composition #4;
190F shows particulates from Test Cycle 6, Standard CA #2 Diesel fuel; and
where 190F shows some alteration of the filter sample due to reflection of the plastic filter casing.

DETAILED DESCRIPTION OF THE INVENTION
AND PREFERRED EMBODIMENTS

Definitions:

As used herein:

5 "Co-solvent alcohol" refers to water-soluble alcohol such as methanol, ethanol, propanol, butanol, pentanol or hexanol. Methanol and/or ethanol are preferred. Anhydrous or 5% aqueous ethanol with methanol 1-10% is more preferred, and anhydrous or 5% aqueous ethanol denatured with isopropanol or butanol about 1-10% by volume is especially preferred.

10 "Ethoxylated alcohols" refer to long-chain fatty alcohols having from between about 12 to 18 carbon atoms, which have an ethylene oxide add-on of less than 5 moles. C12 through C16 fatty alcohols with an ethylene oxide add-on of less than five are preferred, and C12 through C16 fatty alcohols with an ethylene oxide add-on of 3 is most preferred. "Fatty acid" refers to alkyl, alkenyl and alkynyl acids having about 10 to 24
15 carbon atoms, and preferably about 10 to 18 carbon atoms. Linoleic and oleic acids are preferred.

"Fuel" refers to conventional liquid fuel used in burning (usually to produce power, but also to produce heat) and in various internal combustion engines. Liquid fuels include but are not limited to fossil derived fuels such as diesel fuel, heating oil, jet fuel, kerosene,
20 coal slurry, gasoline, combinations thereof and the like. Distilled liquids derived from renewable resources such as vegetable oils optionally are useful as a combustible fuel. These include but are not limited to oils from soybeans, tall, safflower, sunflower, linseed, cottonseed, corn, rapeseed and the like. Diesel fuel is preferred.

"Liquid fuel hydrocarbons" refers to hydrocarbons which form the continuous
25 phase are mixtures of hydrocarbons, such as those refined (distilled) from fossil fuel, including crude petroleum or coal. Coal slurries (liquids) are part of the present hydrocarbon fuel. Diesel fuel hydrocarbons are preferred, however, it is recognized that the invention includes any distilled liquid fuel which forms a microemulsion with the additive, such as jet fuel, fuel oil, gasoline, and the like.

30 "Surfactant portion" refers to those components that generally contribute to reducing surface tension of the water and oil phases, allowing a microemulsion to form. In the present invention, these components are some water-soluble alcohols, water-

insoluble alcohols, ethoxylated alcohols, and fatty acids partially neutralized with a nitrogen base.

"Viscosity similar to a liquid fossil fuel" refers to the change in viscosity that occurs when the additive of the present invention is mixed with a liquid fossil fuel. The viscosity
5 of the additive/fuel is within $\pm 10\%$, preferably within $\pm 5\%$ and more preferably between about $\pm 2\%$ of the original viscosity of the fuel.

"Volatile source of basic nitrogen" refers to nitrogen compounds that, when in the presence of fatty acids produce an exothermic reaction, partially neutralizing the fatty acids, forming ammonium salts and creating an anionic surfactant. Sodium and potassium
10 compounds will also create an anionic surfactant through partial neutralization of fatty acids, but do not fall within the EPA CHON classification, and are metal elements that cannot be used in fuel additives because they form toxic metal contaminants during combustion. Aqueous ammonia, or urea dissolved in water or ethanol, are preferred, and BAUM A 26° aqueous ammonia is most preferred.

15 "Water-insoluble alcohol" refers to those alkyl, alkenyl or alkynyl alcohols (all isomers) having 6 to 12 carbon atoms and a water solubility of less than about 1 g/100 ml at 20°C. Alkyl alcohols between about 6 and 18 carbon atoms are preferred, and those having between 6 to 12 carbon atoms are more preferred. Most preferred alkyl alcohols are normal alcohols having 8 to 10 carbon atoms. Octanol is especially preferred.

20 "Water-soluble portion" refers to those components that generally contribute to fuel oxygenation and have characteristic solvent or detergent qualities that contribute to cleaner burning. In the present invention, these components are water-soluble alcohols (all isomers) and water.

Additional aspects of the invention follow and include;

25 In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble
30 alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or

298

unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or between about 6 and 12 carbon atoms, or between about 8 and 10 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of
5 alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected
10 from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein components a and one or more of b, c, d, and e, when combined with
15 mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 95:5 to 99:1 by volume.

In another aspect, the present invention relates to an additive composition for a
combustible fuel, to utilize readily available and renewable resources and produce
20 improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

25 b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or between about 6 and 12 carbon atoms, or between about 8 and 10 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of
30 alcohols having between 6 and 18 carbon atoms, ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines
5 are excluded;

wherein components a and one or more of b, c, d, and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 90:10 to 99:1 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble
15 alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution, and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or between about 6 and 12 carbon atoms, or between about 8 and 10 carbon
20 atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

25 d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines
30 are excluded;

wherein components a and one or more of b, c, d and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel:

additive ranges from about 80:20 to 99:1 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or preferably between about 6 and 12 carbon atoms, or more preferably between about 8 and 10 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded;

wherein components a and one or more of b, c, d and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 60:40 to 99:1 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or preferably between about 6 and 12 carbon atoms, or more preferably between about 8 and 10 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein components a and one or more of b, c, d, and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 50:50 to 99:1 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or between about 6 and 12 carbon atoms, or between about 8 and 10 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl,

alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded;

wherein components a and one or more of b, c, d and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 1:99 to 50:50 by volume.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive/fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or preferably between about 6 and 12 carbon atoms, or more preferably between about 8 and 10 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded;

wherein the combustible fuel is any conventional or synthetic combustible fuel.

In another aspect, the present invention relates to an additive composition for a

combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or preferably between about 6 and 12 carbon atoms, or more preferably between about 8 and 10 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein the combustible fuel is a fossil fuel such oil, jet fuel, kerosene, other distillate fuels, coal as Diesel fuel, heating slurry, gasoline or combinations thereof.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or between about 6 and 12 carbon atoms, or between about 8 and 10 carbon atoms;

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c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein the combustible fuel is a renewable oil, such as triglycerides from any feedstock, esterification products, waste vegetable oils, tallow, tall oils or combinations thereof.

In another aspect, the present invention relates to an additive composition for a combustible fuel, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which additive or fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or between about 6 and 12 carbon atoms, or between about 8 and 10 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines

are excluded;

wherein the combustible fuel is other alcohols, such as water-insoluble alcohols which are clear liquid at room temperature, having between about 6 and 12 carbon atoms, and long-chain saturated fatty alcohols which are solid at room (ambient) temperature, having between about 13 and 18 carbon atoms.

In another aspect, the present invention relates to an additive composition for a combustible fuel, which may also be used as a fuel composition, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms, or between about 6 and 12 carbon atoms, or between about 8 and 10 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl ethyl n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein the above composition comprises the total combustible fuel and the ratio of the other combustible fuels: above composition is 0:100.

ASPECT FOR CO-SURFACTANTS AND CO-SOLVENTS

In another aspect, the present invention relates to an additive composition for a combustible fuel to produce improved combustion and reduced smoke and particulate production of the combusted fuel, which additive composition comprises:

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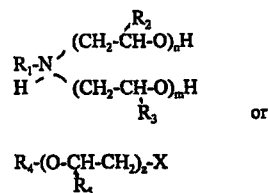
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- a. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms;
- b. at least one cosurfactant selected from the group consisting of clear liquid alcohols having from about 6 and 12 carbon atoms;
- 5 c. at least one cosolvent as a water soluble alcohol selected from the group consisting of methanol, ethanol, propanol, butanol and pentanol;
- d. optionally water; and
- e. a source of nitrogen in an anhydrous state or as any aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl
- 10 hydrazine, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein components a to e when combined with mixing with said combustible fuel form a clear stable micro-emulsion having a viscosity similar to that of the liquid

15 combustible fuel,

wherein the additive composition optionally excludes ethylene glycol, glycerine, polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, or emulsifiers of the general formula:



wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or R_4 is alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or

30 H; R_2 , R_3 and R_3 each independently represent a methyl group or H, n plus m is a number from 1 to 20; z is a number from 0 to 15; and X is $-COO(-)$ or $-OCH_2COO(-)$, wherein, substituents R_2 , R_3 and R_3 is the same or different in different monomer units

35 of each chain, and optionally other organic diacids are excluded.

ASPECT BY PARTS

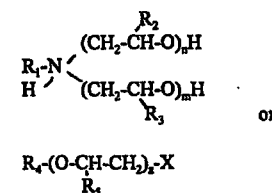
In another aspect, the present invention relates to an additive composition for a combustible fuel to produce improved combustion and reduced smoke and particulate production of the fuel, which additive comprises a composition of components:

- 5 a. a fatty acid of the structure $R-(C=O)-OH$, where R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms is present in between about 15 and 60 parts by volume;
- b. a clear water-insoluble liquid alcohol having from between about 6 and 12 carbon atoms present in between about 5 to 30 parts by volume;
- 10 c. water soluble alcohol selected from methanol or ethanol which in between about 8 to 40 parts by volume;
- d. ammonia sufficient to neutralize between about 40 to 70 by volume the fatty acid of subpart a; and
- e. water which is present in between about 2 and 22 parts by volume;

15 wherein components a to e when combined with mixing with a liquid fuel form a clear stable microemulsion,

wherein the additive composition optionally excludes ethylene glycol, glycerine, polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general

20 formula:



wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or

30 R_4 is alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or H; R_2 , R_3 and R_3 each independently represent a methyl group or H, n plus m is a number from 1 to 20; z is a number from 0 to 15; and X is $-COO(-)$ or $-OCH_2COO(-)$, wherein, substituents

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R_2 , R_3 and R_4 are also different in different monomer units of each chain, and optionally other organic diacids are excluded.

Preferably the fuel/additive is in a ratio to produce a water-in-oil (w/o) emulsion, i.e., between about 50:50 to 95:5, more preferably between about 65:35 to 90:10, and most preferably between about 80:20 to 85:15.

ASPECT BY PARTS II

In another aspect, the present invention relates to an additive composition for a combustible fuel to produce improved combustion and reduced smoke and particulate production of the fuel, which additive comprises a composition of components:

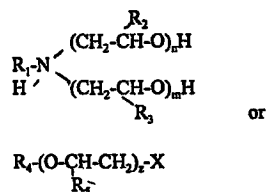
a. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms is present in between about 15 and 60 parts by volume;

b. at least one alcohol selected from the group consisting of methanol, ethanol, propanol, butanol, and pentanol and clear liquid alcohols having from between about 6 and 12 carbon atoms, is present in between about 18 and 75 parts by volume, where methanol is combined with at least one other alcohol;

c. water which is present in between about 2 and 32 parts by volume; and

d. ammonia sufficient to neutralize between about 40 to 70 percent of the fatty acid of subpart a;

wherein the additive composition optionally excludes ethylene glycol, glycerine, polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general formula:



wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain

or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl)

or R_4 is alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or H; R_2 , R_3 and R_5 each independently represent a methyl group or H, n plus m is an integer from 1 to 20; is an integer from 0 to 15; and X is $-COO(-)$ or $-OCH_2COO(-)$, wherein, substituents R_2 , R_3 and R_5 are different in different monomer units of each chain, and optionally other organic diacids are excluded.

Preferably the fuel/additive is in a ratio to produce a water-in-oil (w/o) emulsion, i.e., between about 50:50 to 95:5, more preferably between about 65:35 to 90:10, and most preferably about 80:20 to 85:15 by volume.

10 ASPECT WHERE UREA REPLACES AMMONIA

In another aspect, the present invention relates to an additive composition for a combustible fuel to produce improved combustion and reduced smoke and particulate production of the fuel, which additive comprises a composition of components:

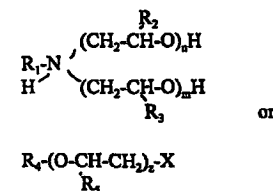
a. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms is present in between about 15 and 60 parts by volume;

b. at least one alcohol selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol and clear liquid alcohols having from between about 6 and 12 carbon atoms, is present in between about 18 and 75 parts by volume, where methanol is combined with at least one other alcohol;

c. water which is present in between about 2 and 32 parts by volume; and

d. urea sufficient to neutralize between about 40 to 70 percent of the fatty acid of subpart a;

wherein the additive composition optionally excludes ethylene glycol, glycerine, polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general formula:



wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or R_4 is alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain
 5 or H; R_2 , R_3 and R_5 each independently represent a methyl group of H, n plus m is a number from 1 to 20; z is a number from 0 to 15; and X is $-\text{COO}(-)$ or $-\text{OCH}_2\text{COO}(-)$, wherein, substituents R_2 , R_3 and R_5 the same or different in different monomer units of each chain, and optionally other organic diacids are excluded.

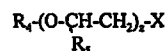
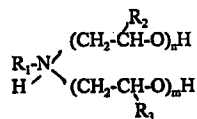
Preferably the fuel/additive is in a ratio to produce a water-in-oil (w/o)
 10 emulsion, i.e., between about 50:50 to 95:5, more preferably between about 65:35 to 90:10, and most preferably about 80:20 to 85:15.

ASPECT WHERE ETHANOL IS THE ONLY ALCOHOL

In another aspect, the present invention relates to an additive composition for a
 15 combustible fuel to produce improved combustion and reduced smoke and particulate production of the fuel, which additive comprises a composition of components:

- a. a fatty acid of the structure $\text{R}-(\text{C}=\text{O})-\text{OH}$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms is present in between about 15 and 60 parts by volume;
- 20 b. ethanol is present in between about 18 and 75 parts;
- c. water which is present in between about 2 and 32 parts by volume; and
- d. urea and/or ammonia sufficient to neutralize between about 40 to 70 percent of the fatty acid of subpart a;

wherein the additive composition optionally excludes ethylene glycol, glycerine,
 25 polyethylene, polyoxyethylene, polyoxypropylenes, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general formula:



wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or R_4 is also can be alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or H; R_2 , R_3 and R_5 each independently represent a methyl group or H, n
 5 plus m is to be a number from 1 to 20; z can be a number from 0 to 15; and X is $-\text{COO}(-)$ or $-\text{OCH}_2\text{COO}(-)$, wherein, substituents R_2 , R_3 and R_5 are the same or different in different monomer units of each chain, and optionally other organic diacids are excluded.

Preferably the fuel/additive is a ratio to produce a water-in-oil (w/o) emulsion,
 10 i.e., between about 65:35 to 90:10, and most preferably about 80:20 to 85:15 by volume.

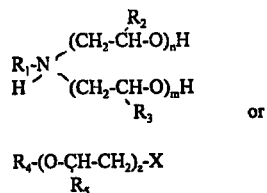
ASPECT WHERE C6-C12 ALCOHOLS ARE THE ONLY ALCOHOLS PRESENT

In another aspect, the present invention relates to an additive composition for a
 15 combustible fuel to produce improved combustion and reduced smoke and particulate production of the fuel, which additive comprises a composition of components.

- a. a fatty acid of the structure $\text{R}-(\text{C}=\text{O})-\text{OH}$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms is present in between about 15 and 60 parts by volume;
- 20 b. at least one alcohol selected from the group consisting of clear liquid alcohols having from between about 6 and 12 carbon atoms, is present in between about 18 and 75 parts by volume;
- c. water which is present in between about 2 and 32 parts by volume; and
- d. urea and/or ammonia sufficient to neutralize between about 40 to 70 percent of the fatty acid of subpart a;
- 25

wherein the additive composition optionally excludes ethylene glycol, glycerine, polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general formula:

37



wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or R_4 is alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or H; R_2 , R_3 and R_5 each independently represent a methyl group or H, n plus m is a number from 1 to 20; z is a number from 0 to 15; and X is $-\text{COO}(-)$ or $-\text{OCH}_2\text{COO}(-)$, wherein, substituents R_2 , R_3 and R_5 are the same or different in different monomer units of each chain, and optionally other organic diacids are excluded.

Preferably the fuel/additive is in a ratio to produce a water-in-oil (w/o) emulsion, i.e., between about 50:50 to 95:5, more preferably between about 65:35 to 90:10, and most preferably about 80:20 to 85:15 by volume.

ASPECT WHERE FATTY ALCOHOLS ARE INTRODUCED USING FOSSIL FUEL AS A CO-SOLVENT

In another aspect, the present invention relates to an additive composition for a combustible fuel to produce improved combustion and reduced smoke and particulate production of the fuel, which additive comprises a composition of components:

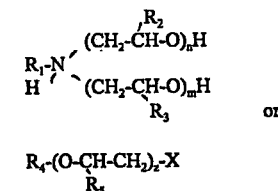
- a. a fatty acid of the structure $\text{R}-(\text{C}=\text{O})-\text{OH}$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms is present in between about 15 and 60 parts by volume;
- b. at least one alcohol selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol and clear liquid alcohols having from between about 6 and 12 carbon atoms, is present in between about 12 and 50 parts by volume, where methanol is combined with at least one other alcohol;
- d. water present in between about 2 and 32 parts by volume;
- e. urea, ammonia or combinations thereof sufficient to neutralize between about 40 to 70 percent of the fatty acid of subpart a;
- f. at least one long-chain fatty alcohol selected from the group consisting

38

of alcohols which are solid at room temperature, having from between about 13 and 18 carbon atoms in between about 6 and 25 parts by volume;

- g. a co-solvent of fossil fuel in between about 6 and 25 parts by volume; wherein the additive composition optionally excludes ethylene glycol, glycerine,

polyethylene, polypropylene, metals, metal compounds, compounds of phenanthrene, and emulsifiers the general formula:



wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or R_4 is also can be alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or H; R_2 , R_3 and R_5 each independently represent a methyl group or H, n plus m is a number from 1 to 20; z is a number from 0 to 15; and X is $-\text{COO}(-)$ or $-\text{OCH}_2\text{COO}(-)$, wherein, substituents R_2 , R_3 and R_5 are the same or different in different monomer units of each chain, and optionally other organic diacids are excluded.

Preferably the fuel/additive is in a ratio to produce a water-in-oil (w/o) emulsion, i.e., between about 50:50 to 95:5, more preferably between about 65:35 to 90:10, and most preferably about 80:20 to 85:15 by volume.

ASPECT WHERE FATTY ALCOHOLS ARE INTRODUCED USING A NON-IONIC SURFACTANT

In another aspect, the present invention relates to an additive composition for a combustible fuel to produce improved combustion and reduced smoke and particulate production of the fuel, which additive comprises a composition of components:

- a. a fatty acid of the structure $\text{R}-(\text{C}=\text{O})-\text{OH}$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms is present in between about 15 and 60 parts by volume;
- b. at least one alcohol selected from the group consisting of methanol,

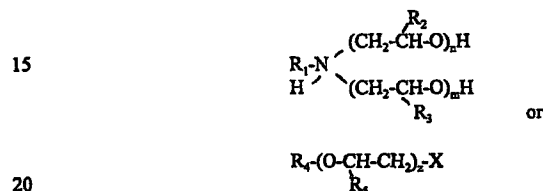
ethanol, propanol, butanol, pentanol and clear liquid alcohols having from between about 6 and 12 carbon atoms, is present in between about 12 and 50 parts by volume, where methanol is combined with at least one other alcohol;

d. water which is present in between about 2 and 32 parts by volume;

5 e. urea and/or ammonia sufficient to neutralize between about 40 to 70 percent of the fatty acid of subpart a;

f. at least one long-chain fatty alcohol selected from the group consisting of alcohols which are solid at room temperature, having from between about 13 and 18 carbon atoms is present in between about 6 and 25 parts;

10 wherein the additive composition optionally excludes polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general formula:



wherein R₁ and R₄ each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or R₄ is alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or
 25 H; R₂, R₃ and R₅ each independently represent a methyl group or H, n plus m is an integer from 1 to 20; z is an integer from 0 to 15; and X is -COO(-) or -OCH₂COO(-), wherein, substituents R₂, R₃ and R₅ are the same or different in different monomer units of each chain, and optionally other organic diacids are excluded.

Preferably the fuel/additive is in a ratio to produce a water-in-oil (w/o)
 30 emulsion, i.e., between about 50:50 to 95:5, more preferably between about 65:35 to 90:10, and most preferably about 80:20 to 85:15 by volume.

ASPECT WHERE FATTY ALCOHOLS AND NON-IONIC SURFACTANTS ARE INTRODUCED USING FOSSIL FUEL AS A CO-SOLVENT

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The present invention relates to an additive composition for a combustible fuel

to produce improved combustion and reduced smoke and particulate production of the combusted fuel, which additive composition comprises:

a. a fatty acid of the structure R-(C=O)-OH, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms;

5 b. at least one alcohol selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol and clear liquid alcohols having from between about 6 and 12 carbon atoms, where methanol is always be combined with at least one other alcohol;

c. water; and

10 d. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

15 e. optionally, at least one long-chain fatty alcohol selected from the group consisting of alcohols which are solid at room temperature, having from between about 13 and 18 carbon atoms;

f. optionally, an ethoxylated non-ionic surfactant wherein the ethylene oxide condensation product is formed with a fatty alcohol of the formula:



20 wherein R₆ is a long-chain, saturated or unsaturated hydrocarbon radical containing 12 to 18 carbon atoms and n is an integer from 1 to 4;

g. optionally, a liquid fossil fuel.

wherein components a to g when combined with mixing with said combustible
 25 fuel form a clear stable micro-emulsion having a viscosity similar to a liquid combustible fuel,

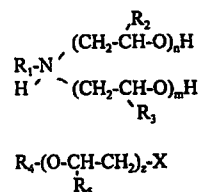
wherein the additive composition optionally excludes ethylene glycol, glycerine, polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general

30 formula:

302

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41



10 wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or R_4 also can be alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or H; R_2 , R_3 and R_5 each independently represent a methyl group of H, n plus m is to be a number from 1 to 20; z can be a number from 0 to 15; and X is -

15 $\text{COO}(-)$ or $-\text{OCH}_2\text{COO}(-)$, wherein, substituents R_2 , R_3 and R_5 can also be different in different monomer units of each chain, and optionally other organic diacids are excluded.

Compositions of the present invention are easily used in place of the corresponding hydrocarbon fuels without substantial changes in combustion apparatus

20 or equipment.

Even with the components used herein there are rules and limitations. For example:

Too much methanol causes dissolving of sensitive engine or fuel system parts.

Too much water causes poor combustion, possible corrosion.

25 Too much of any water-soluble portion causes no stability.

Too much water-insoluble alcohol causes poor viscosity.

Too much ethoxylated alcohol causes poor viscosity and poor combustion.

Too much fatty acid causes poor viscosity, fatty acid degradation.

Too much ammonia causes no stability of the microemulsion.

30 Too much of any surface-active portion causes poor viscosity, and factors prohibitively in end-use costs.

On the other hand:

Too little water-soluble alcohol causes poor viscosity and reduces emissions improvements.

35 Too little water causes reduced emissions improvements;

42

Too little surfactant portion causes no stability; and

Too little water-insoluble alcohol in relation to ethoxylated alcohols or fatty acids causes poor viscosity.

The stability of the fuel/additive emulsions of the present invention at lower

5 temperatures from about -20°C to $+70^\circ\text{C}$. Alternatively, the upper limit is about 20°C (preferably about 20°C) lower than the boiling point of the fuel.

The stable fuel/additive emulsions have improved long term storage properties.

The appearance of the fuel/additive emulsion is as a clear liquid having the expected properties of a water-in-oil without microemulsion. All of the components of

10 the fuel/additive emulsion are known and are preparable from conventionally known starting materials. Most, if not all, are available from commercial sources.

Some preferred compositions of the present invention include but are not limited to those:

wherein Example A below is repeated except that the additive composition

15 amounts are replaced to be the additive composition as follows:

linoleic acid, or oleic acid, or both; 16-36 parts by volume

octanol; 6-32 parts by volume

methanol; 12-28 parts by volume

water; 0.5-16 parts by volume

20 aqueous ammonia or urea 0.3-6 parts by volume

where the preferred fuel is Diesel fuel, the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C .

25 wherein Example A below is repeated except that the additive composition amounts are replaced to be the additive composition as follows:

linoleic acid, or oleic acid, or both; 16-36 parts by volume

2-ethyl hexanol-1, or octanol or octadecanol,

or decanol; 6-32 parts by volume

30 methanol; 12-28 parts by volume

water; 0.5-16 parts by volume

aqueous ammonia or urea 0.3-6 parts by volume

100

where the preferred fuel is Diesel fuel, the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C.

- 5 wherein Example A below is repeated except that the additive composition amounts are replaced to be the additive composition as follows:

linoleic acid, or oleic acid, or both; 16-36 parts by volume
2-ethyl hexanol-1, or octanol or octadecanol,
or decanol; 6-32 parts by volume

- 10 methanol, or ethanol, or both
or methanol and/or ethanol
with iso-propanol or butanol; 12-28 parts by volume
water; 0.5-16 parts by volume
aqueous ammonia or urea 0.3-6 parts by volume

- 15 where the preferred fuel is Diesel fuel, the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C.

- 20 wherein Example A below is repeated except that the additive composition amounts are replaced to be the additive composition as follows:

linoleic acid, or oleic acid, or both; 16-36 parts by volume
ethoxylated alcohol with 12-18 carbons
and ethylene oxide ending of less than 5; 2-10 parts by volume

- 25 2-ethyl hexanol-1, or octanol or octadecanol,
or decanol; 6-32 parts by volume

methanol, or ethanol, or both
or methanol and/or ethanol
with iso-propanol or butanol; 12-28 parts by volume
water; 0.5-16 parts by volume

- 30 aqueous ammonia or urea 0.3-6 parts by volume

where the preferred fuel is Diesel fuel, kerosene, or heating oil, the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear

microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C.

wherein Example A below is repeated except that the additive composition amounts are replaced to be the additive composition as follows:

- 5 ethoxylated alcohol with 12-18 carbons
and ethylene oxide ending of less than 5; 2-10 parts by volume
2-ethyl hexanol-1, or octadecanol,
or decanol; 6-32 parts by volume
ethanol, or ethanol with methanol,
10 or ethanol with iso-propanol or butanol; 12-32 parts by volume
water; 0.5-8 parts by volume

where the preferred fuel is Diesel fuel or gasoline, fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear microemulsion composition that remains stable over time, up to 6 months or longer,

- 15 and during and after storage at a temperature of -20°C.

wherein Example A below is repeated except that the additive composition amounts are replaced to be the additive composition as follows:

- 20 ethoxylated alcohol with 12-18 carbons
and ethylene oxide ending of less than 5; 6-32 parts by volume
ethanol, or ethanol with methanol,
or ethanol with iso-propanol or butanol; 12-32 parts by volume
water; 0.5-8 parts by volume

where the preferred fuel is Diesel fuel or gasoline, fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear

- 25 microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C.

wherein Example A is repeated except that the additive composition amounts are replaced to be the additive composition as follows:

- 2-ethyl hexanol-1, or octanol or octadecanol,
30 or decanol; 12-32 parts by volume
ethanol, or ethanol with methanol,
or ethanol with iso-propanol or butanol; 12-32 parts by volume

water; 0.5-4 parts by volume

where the preferred fuel is Diesel fuel or gasoline, fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C.

It is important to understand that the present invention is a significant advance in additives designed to introduce water-soluble components into Diesel fuel and other fossil fuels.

Although it is generally understood that the addition of water-soluble elements into fossil fuels would have a positive oxygenating effect; fossil fuels are, generally, chemically hydrophobic, meaning they will not readily absorb or mix with water and/or water-soluble components.

Gasoline will tolerate certain levels of ethanol and methanol, which are water-soluble, but will not tolerate high levels of methanol, will not tolerate any level of water, and will, in the presence of water, exhibit immediate phase separation without some chemical or mechanical means of breaking surface tension to produce a stable solution or emulsion.

Less-refined fossil fuels such as Diesel fuel and kerosene, are especially hydrophobic, and will not tolerate any level of water-soluble alcohol or water, and will, in the presence of either, exhibit immediate phase separation without some chemical or mechanical means of breaking surface tension to produce a stable solution or emulsion.

It is important to understand that many methods have been tried to overcome the problem of phase separation between fossil fuels and water-soluble components.

Prior art, such as Wenzel et al, US Patent 4,083,698, successfully produces stable microemulsions with water and methanol, but utilizes high concentrations of non-ionic surfactants with 5,7,9 and up to 20 moles of ethylene oxide, or polyethylene, polyoxyethylene, or polyoxypropylene molecules. While these create stable microemulsions, viscosity is adversely affected, producing compositions that are more viscous than Diesel fuel, which poses potential problems in adequate fuel flow during use in an engine.

The above ethylene, polyethylene, polyoxyethylene, or polyoxypropylene additions are also largely incombustible, which poses the immediate problem of increased

exhaust smoke when not specifically limited or eliminated entirely from compositions for use as fuel.

Other products currently used or under investigation for the purpose of introducing water-soluble elements into fossil fuel include Methyl Tertiary Butyl Ether (MTBE) and Methyltetrahydrofuran.

MTBE, which is currently used in many states as a gasoline additive, is a significant alteration of the chemical composition of methanol, making it 'oleophilic,' so that it will mix with and can be used to oxygenate gasoline. The process of producing MTBE, however, also alters the biodegradability of the methanol, and has been shown to filtrate through to groundwater and contaminate drinking water supplies.

The present invention can be used to introduce water-soluble alcohols into gasoline to achieved oxygenation with no toxic contamination of the air or water supplies.

Methyltetrahydrofuran, which is currently under study as a Diesel fuel additive, is another significant alteration of methanol, increasing its solvent qualities. This methanol compound breaks surface tension between Diesel fuel and ethanol, making it possible to utilize ethanol for its oxygenating properties.

However, methyltetrahydrofuran is an extremely aggressive solvent that melts steel. Its use in engines as a fuel additive poses a very high risk of causing damage to internal engine and sensitive fuel system parts.

The present invention can be used to introduce water soluble alcohols and water into Diesel fuel with no damage to engine or fuel system parts.

Even currently used ethanol, denatured with methanol, poses a problem when used to oxygenate gasoline because methanol especially attracts water to the mixture, promoting phase separation; and because methanol is a much stronger solvent than ethanol (about 10 times stronger) which has been shown to adversely affect pipelines through which gasoline is shipped to many suppliers.

The present invention can be used to introduce ethanol into gasoline to achieve oxygenation, with no phase separation, damage to pipelines, engines or fuel systems, and with no toxic contamination of the air or water supplies.

It is also important to understand that, in addition to fossil fuel oxygenation, the present invention is a significant advance in additives designed to introduce renewable

and readily-available resources into fossil fuels.

It is generally understood that successful introduction into fossil fuels of oils and alcohols derived from bio-mass sources would have a positive effect on extending dwindling fuel supplies by fully utilizing readily-available resources that are also

5 renewable.

Significant attempts have been made to introduce ethanol, which can be derived from bio-mass sources, into fossil fuels, as described above.

Significant attempts have also been made to introduce vegetable oil products, such as soy and rapeseed oils, into fossil fuels, specifically for the purpose of utilizing

10 these oils.

A product commercially known as "Biodiesel" is currently being developed and tested in transit bus lines, marine diesel engines, and industrial furnaces. Biodiesel is made from methyl esters, a process by which methanol and vegetable oils are chemically bonded.

15 However, methyl esters solidify at relatively high temperatures. Biodiesel must be heat-jacketed for storage at temperatures of less than 32°F, and no practical solution has been found for the problem of additive gelling in fuel tanks when ambient temperatures drop below freezing.

20 It is important to understand that the present invention utilizes components, such as fatty acids, that can be derived from a wide range of renewable sources such as soy, rapeseed, peanut, safflower, tall(tree) oil, and tallow, with no compromise to additive viscosity at high or low temperatures.

The compositions of the invention also utilize water-insoluble alcohols that can be derived from either fossil (coal) or renewable sources such as palm or coconut. The

25 present invention also utilizes water-soluble alcohols, such as ethanol, that can also be derived from fossil sources (such as coal), or from bio-mass sources such as corn or surplus or damaged crops.

It is important to understand that the wide range of possible sources from which components for the present invention can be derived is a significant advance in additive

30 technologies designed to incorporate renewable resources into fossil fuels. Many present technologies rely on one or two sources, such as soy or canola (rapeseed) oils, which presently are prohibitively expensive and hinder commercially successful

utilization. Biodiesel is one such technology.

Other technologies rely on inexpensive components, such as methanol, as the source from which components are derived. However, methanol derivatives tend to be toxic, or non-biodegradable, or chemically aggressive, or all of the above. MTBE and

5 methyltetrahydrofuran are such examples.

It is possible to derive components for the present invention from a wide selection of renewable feedstocks, such as tall oil, tallow, soy, canola, waste oils, cottonseed, corn, peanut, safflower, coconut and palm oils, as well as crushed waste, surplus, or damaged crops.

10 But it is also important that several of the preferred embodiments of the present invention can be derived almost entirely from coal, and still produce clear, stable microemulsions that oxygenate fossil fuels.

This provides an essential link, economically, for successfully introducing alcohol/water-based oxygenators that can also be made entirely from renewable

15 sources at any time that positive economic and/or political factors make them commercially viable.

The present invention is, among other things, a 'roadmap' for the successful introduction of renewable fuels, by making it possible to mix relatively high-cost renewable components with lower-cost fossil-based components in proportions that

20 optimize economic and environmental benefits.

The present invention makes it possible to utilize all of the above-mentioned components in such a way that the resulting compositions will maintain, and in some cases improve, viscosity levels of Diesel and other fossil fuels.

The present invention also makes it possible to utilize all of the above-

25 mentioned components in such a way that the resulting compositions will not pollute the environment, or harm engines or fuel systems.

The present invention also makes it possible to utilize all of the above-mentioned components in such a way that the resulting compositions maintain good combustion characteristics, and, when properly mixed with Diesel and other fossil

30 fuels, will improve combustion and reduce toxic exhaust emissions.

Some preferred compositions of the present invention include but are not limited to those:

wherein Examples 1-7 are repeated except that the additive composition amounts are replaced to be the additive composition as follows:

2-ethyl hexanol- 1 or octanol
or octadecanol, or decanol; 12-32 parts by volume
5 ethanol, or ethanol with methanol,
or ethanol with iso-propanol or butanol; 12-32 parts by volume
water 0.5-4 parts by volume

where the fuel/additive ratio is about 80:20 to 95:5 and the result of combustion of the resulting fuel additive composition is improved combustion, reduced carbon
10 buildup inside the engine, reduced smoke, particulates, and noxious gases, reduced unburnt hydrocarbon emissions and improved fuel consumption efficiency.

wherein Examples 1-7 are repeated except that the additive composition amounts are replaced to be the additive composition as follows:

ethoxylated alcohol with 12-18 carbons
15 and ethylene oxide ending of less than 5; 6-32 parts by volume
ethanol, or ethanol with methanol,
or ethanol with iso-propanol or butanol; 12-32 parts by volume
water 0.5-8 parts by volume

where the fuel/additive ratio is about 80:20 to 95:5 and the result of combustion
20 of the resulting fuel additive composition is improved combustion reduced carbon buildup inside the engine, reduced smoke, particulates, and noxious gases, reduced unburnt hydrocarbon emissions and improved fuel consumption efficiency.

In another aspect Examples 1-7 are repeated except that the additive composition amounts are replaced to be the additive composition as follows:

25 ethoxylated alcohol with 12-18 carbons
and ethylene oxide ending of less than 5; 2-10 parts by volume
2-ethyl hexanol-1, or octanol,
or octadecanol, or decanol; 6-32 parts by volume
ethanol, or ethanol with methanol, or
30 ethanol with iso-propanol or butanol; 12-32 parts by volume
water 0.5-8 parts by volume

where the fuel/additive ratio is about 80:20 to 95:5 and the result of combustion

of the resulting fuel additive composition is improved combustion, reduced carbon buildup inside the engine, reduced smoke, particulates, and noxious gases, reduced unburnt hydrocarbon emissions and improved fuel consumption efficiency.

In another aspect Examples 1, 2, 3 or 7 below are repeated except that the
5 additive composition amounts are replaced to be the additive composition as follows:

linoleic acid, or oleic acid, or both; 16-36 parts by volume
ethoxylated alcohol with 12-18 carbons
and ethylene oxide ending of less than 5; 2-10 parts by volume
10 2-ethyl hexanol-1, or octanol,
or octadecanol, or decanol; 6-32 parts by volume
methanol, or ethanol, or both,
or methanol and/or ethanol
with iso-propanol or butanol; 12-28 parts by volume
15 water; 0.5-16 parts by volume
aqueous ammonia or urea 0.3-6 parts by volume

where the fuel/additive ratio is about 80:20 to 95:5 and the result of combustion of the resulting fuel additive composition is improved combustion, reduced carbon
20 buildup inside the engine, reduced smoke, particulates, and noxious gases, reduced unburnt hydrocarbon emissions and further improved fuel consumption efficiency.

In another aspect Examples 1, 2, 3 or 7 below are repeated except that the additive composition amounts are replaced to be the additive composition as follows:

linoleic acid, or oleic acid, or both; 16-36 parts by volume
25 2-ethyl hexanol-1, or octanol,
or octadecanol, or decanol; 6-32 parts by volume
methanol, or ethanol, or both,
or methanol and/or ethanol
with iso-propanol or butanol; 12-28 parts by volume
water; 0.5-16 parts by volume
30 aqueous ammonia or urea; 0.3-6 parts by volume

where the fuel/additive ratio is about 80:20 to 95:5 and the result of combustion of the resulting fuel additive composition is improved combustion, reduced carbon

buildup inside the engine, reduced smoke, particulates, and noxious gases, reduced unburnt hydrocarbon emissions and further improved fuel consumption efficiency.

In another aspect Examples 1, 2, 3 or 7 below are repeated except that the additive composition amounts are replaced to be the additive composition as follows:

- | | | |
|----|--|------------------------|
| 5 | linoleic acid, or oleic acid, or both; | 16-36 parts by volume |
| | methanol, or ethanol, or both, | |
| | or methanol and/or ethanol with | |
| | iso-propanol or butanol; | 12-28 part by volume |
| | water; | 0.5-16 parts by volume |
| 10 | aqueous ammonia or urea; | 0.3-6 parts by volume |

where the fuel/additive ratio is about 80:20 to 95:5 and the result of combustion of the resulting fuel additive composition is improved combustion, reduced carbon buildup inside the engine, reduced smoke, particulates, and noxious gases, reduced unburnt hydrocarbon emissions and further improved fuel consumption efficiency.

- 15 In another aspect Examples 1, 2, 3 or 7 below are repeated except that the additive composition amounts are replaced to be the additive composition as follows:

- | | | |
|----|--|---------------------------|
| | fatty acid (linoleic acid) | 40 to 44 parts by volume; |
| | water-insoluble alcohol (octanol) | 20 to 22 parts by volume; |
| | water-soluble alcohol (ethanol denatured | |
| 20 | with 5-10% methanol) | 16 to 18 parts by volume; |
| | water | 4 to 6 parts by volume; |
| | aqueous ammonia (28%) | 4 to 6 parts by volume; |

where the fuel/additive ratio is about 95:5 to 85:15 and the result of combustion of the resulting fuel/additive composition is improved combustion reduced carbon

- 25 buildup inside the engine, and reduced smoke, particulates, and noxious gases.

In another aspect Examples 1, 2, 3 or 7 below are repeated except that the additive composition amounts are replaced to be the additive composition as follows:

- | | | |
|----|--|-----------------------------|
| | fatty acid (linoleic acid) | 34 to 36 parts by volume; |
| | water-insoluble alcohol (octanol) | 16 to 18 parts by volume; |
| 30 | water-soluble alcohol (methanol-denatured) | 20 to 24 parts by volume; |
| | water | 9 to 12 parts by volume; |
| | aqueous ammonia (28%) | 4.6 to 4.9 parts by volume; |

where the fuel/additive ratio is about 90:10 to 75:25 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine, and further reduced smoke, particulates, and noxious gases compared to compositions having a lower additive proportion.

- 5 In another aspect Examples 1, 2, 3 or 7 below are repeated except that the additive composition amounts are replaced to be the additive composition as follows:

- | | | |
|----|--|-----------------------------|
| | fatty acid (linoleic acid) | 28 to 32 parts by volume; |
| | water-insoluble alcohol (octanol) | 10 to 16 parts by volume; |
| | water-soluble alcohol (methanol) + ethanol | 24 to 28 parts by volume; |
| 10 | water | 10 to 15 parts by volume; |
| | aqueous ammonia (28%) | 3.8 to 4.4 parts by volume; |

where the fuel/additive ratio is about 80:20 to 65:35 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine, and reduced noxious gases and remarkably reduced

- 15 smoke and particulate emissions.

In another aspect Examples 1, 2, 3 or 7 below are repeated except that the additive composition amounts are replaced to be the additive composition as follows:

- | | | |
|----|--|-----------------------------|
| | fatty acid (linoleic acid) | 24 to 26 parts by volume; |
| | water-insoluble alcohol (octanol) | 8 to 12 parts by volume; |
| 20 | water-soluble alcohol (methanol) + ethanol | 24 to 28 parts by volume; |
| | water | 10 to 15 parts by volume; |
| | aqueous ammonia (28%) | 3.8 to 4.4 parts by volume; |

where the fuel/additive ratio is about 65:35 to 50:50 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced

- 25 carbon buildup inside the engine, and reduced noxious gases and remarkably reduced smoke and particulate emissions.

It is important to understand that the present invention is a significant advance in additives designed to oxygenate fossil fuels. The selection and use of the components described herein fall within the US EPA 'CHON' classification, meaning they contain

- 30 only carbon, hydrogen, oxygen and nitrogen.

The selection and use of the components described herein are non-toxic compared to fossil fuel, especially Diesel fuel, and are non-toxic and bio-degradeable

compared to other additives such as methyltetrahydrofuran and methyl tertiary butyl ether (MTBE).

The selection and use of the components described herein can be derived entirely from renewable bio-sources, and some may also be derived from coal to offset
5 currently high costs associated with renewable fuels production compared to fossil fuel production.

It is important also to understand that the present invention is a significant advance in additives for fuels for internal combustion engines. The selection and use of the components described herein improve by about 50% or greater reduction of the
10 smoke and particulates produced by incomplete combustion. Specific additive compositions will provide 30%, 40%, 50%, 60%, 70%, 80% or greater reductions in total particulate emissions and 50%, 60%, 70%, 80%, 90% or greater reduction in smoke opacity.

The commercial sources of components can be obtained by referring to
15 Chemical Sources U.S.A. published annually by Directories Publications, Inc. of Boca Raton, Florida. Usually the materials are used in the present invention as received without further purification.

The following Examples are provided to be illustrative and descriptive only. They are not to be construed to be limited in any way.

EXAMPLE 1

COMBUSTION TESTS WITH ADDITIVE COMPOSITION PHOTO DOCUMENTATION OF VISIBLE EXHAUST EMISSIONS

a) A confidential test experiment was performed at the Stockton East Water District, Stockton, California.

25 The engine was a 300 hp V8 Caterpillar Diesel engine (one of four pumping engines at the site).

The additive formulation was by parts by volume:

30 parts linoleic acid
10 parts TERGITOL 1553 (3 moles ethylene oxide 15C alcohol)
30 28 parts methanol
15 parts water
4.1 parts aqueous ammonia

The blend ratio was Diesel fuel: additive of 65:35 by volume.

Forty gallons of the subject additive blend in a 55 gallon drum were lifted by forklift to the level of the far right engine and the fuel pump/line was secured to the fuel drum. The engine was started with fuel/additive blend as its only fuel supply. No
5 changes were made to the engine other than switching the fuel supply.

With reference to Figures 1-6 the experimental results are described.

Figure 1 shows Caterpillar engine used for the test.

Figure 2 shows containers of the additive blends.

Figure 3 shows engine housing building with typical straight diesel fuel startup
10 emissions shown from the left smoke stack.

Figure 4 shows a typical startup from engine using the fuel/additive blend shown from far right smoke stack.

Figure 5 shows typical smoke wisp from two left smoke stacks where straight diesel fuel is being used.

15 Figure 6 shows no visible smoke from the far right smoke stack where the fuel additive blend has been running for approximately 15 minutes. Engine associated with the left smoke stack is not running and far left smoke wisp above the far left dome is from an engine using straight Diesel fuel.

EXAMPLE 2

COMBUSTION TESTS WITH ADDITIVE COMPOSITION 1-MINUTE FILTER SAMPLE COLLECTION OF PARTICULATE EMISSIONS

a) A confidential test experiment was performed at the Stockton East Water District, Stockton, California.

25 The engine was a 360 hp V8 Caterpillar diesel engine (one of four pumping engines at the site).

The additive formulation, was by parts, by volume:

30 parts linoleic acid
10 parts octanol
28 parts methanol
30 15 parts water
4.1 parts aqueous ammonia

The blend ratio was Diesel fuel: additive of 65:35 by volume.

The white cloth-like material used as the filter to collect particulates is a white felt "Classic felt" approximately 8-1/2" wide x 11" long, available from Foss Manufacturing Co., Retail Division, and is also available from Mendel's Far-Out Fabrics, 1556 Haight Street, San Francisco, CA 94117.

5 The properties are as follows:

FELT PROPERTY TABLE

PROPERTY	SPECIFICATION	TEST	METHOD
Fiber	Polyester and/or Acrylic		
10 Width	As requested +/- .5"	ASTM	D461
Weight	5.0 +/- .5 OZ/YD2	FTM N	W503
Thickness	.080" +/- .010"	ASTM	D1777
Tensile Warp @ 10 lb Fill	75 LBS minimum 85 LBS minimum	FTM N	W505
15 Elongation Warp @ 10 lb Fill	25% AVG. 40% AVG.	FTM N	W506
Appearance	To Match Approved Standard	Visual	
Color	To Match Approved Standard	Visual	
Critical	Appearance, Weight and Gauge		

20 The filters were stretched across generally available wooden embroidery hoops approximately 7" in diameter.

These filters are intended as a visual aid to demonstrate smoke and particulate reduction. They are not intended to be used for quantitative (weighed) studies. They provide qualitative comparisons between diesel fuel emissions and emissions from the

25 additive fuel composition.

Forty gallons of the subject additive blend in a 55 gallon drum were lifted by forklift to the level of the far right engine and the fuel pump/line was secured to the fuel drum. The engine was started with fuel/additive blend as its only fuel supply. No changes were made to the engine other than switching the fuel supply.

30 The muffler and exhaust pipe for the engine in Figure 1 are located on the roof of the building which houses the water pumping engines. Each filter sample was held approximately 5-7 inches above the exhaust pipe with a pair of standard long-handled pliers available in a hardware store. All sample collection tests lasted exactly one

minute (60 seconds).

With reference to Figures 7-10 and 11-18, the experimental results are described.

Figures 7-10 show the procedure used for collecting filter samples.

Figures 11-18 show the emission-reduction results.

5 (b) Similarly Example 2(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

fatty acid (linoleic acid)	44 parts by volume;
water-insoluble alcohol (octanol)	22 parts by volume;
water-soluble alcohol (methanol)	18 parts by volume;
10 water	6 parts by volume;
aqueous ammonia (28%)	6 parts by volume;

where the fuel additive ratio is about 95:5 to 85:15 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine and reduced smoke, particulates, and noxious gases.

15 (c) Similarly Example 2(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

fatty acid (linoleic acid)	36 parts by volume;
water-insoluble alcohol (octanol)	18 parts by volume;
water-soluble alcohol (methanol)	24 parts by volume;
20 water	12 parts by volume;
aqueous ammonia	5.5 parts by volume;

where the fuel additive ratio is about 90:10 to 75:25 and the result of combustion of the resulting fuel/additive composition is improved combustion) reduced carbon buildup inside the engine and further reduced smoke, particulates, and noxious gases compared to compositions having a lower additive proportion.

25 (d) Similarly Example 2(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

fatty acid (linoleic acid)	32 parts by volume;
water-insoluble alcohol (octanol)	16 parts by volume;
30 water-soluble alcohol (methanol)	28 parts by volume;
water	15 parts by volume;
aqueous ammonia (28%)	4.9 parts by volume;

where the fuel additive ratio is about 80:20 to 65:35 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine and reduced noxious gases and remarkably reduced smoke and particulate emissions) where the results are essentially the same as represented in Figures 11-18.

(e) Similarly Example 2(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

fatty acid (linoleic acid)	26 parts by volume;
water-insoluble alcohol (octanol)	12 parts by volume;
water-soluble alcohol (methanol)	28 parts by volume;
water	15 parts by volume;
aqueous ammonia (28%)	4.4 parts by volume;

where the fuel additive ratio is about 65:35 to 50:50 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine and reduced noxious gases and remarkably reduced smoke and particulate emissions) where the results are essentially the same as represented in Figures 11 - 18.

(f) Similarly Example 2(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

fatty acid (oleic acid)	40 parts by volume;
water-insoluble alcohol (octanol)	20 parts by volume;
water-soluble alcohol (methanol)	16 parts by volume;
water	4 parts by volume; and
aqueous ammonia (28%)	4 parts by volume,

where the fuel additive ratio is about 95:5 to 85:15 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine and reduced smoke, particulates, and noxious gases.

(g) Similarly Example 2(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

fatty acid (oleic acid)	34 parts by volume;
water-insoluble alcohol (octanol)	16 parts by volume;
water-soluble alcohol (methanol)	20 parts by volume;

water	9 parts by volume;
aqueous ammonia (28%)	4.6 parts by volume,

where the fuel additive ratio is about 90:10 to 75:25 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine and further reduced smoke, particulates, and noxious gases compared to compositions having a lower additive proportion.

(h) Similarly Example 2(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

fatty acid (oleic acid)	28 parts by volume;
water-insoluble alcohol (octanol)	10 parts by volume;
water-soluble alcohol (methanol)	24 parts by volume;
water	10 parts by volume;
aqueous ammonia (28%)	3.8 parts by volume,

where the fuel additive ratio is about 80:20 to 65:35 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine and reduced noxious gases and remarkably reduced smoke and particulate emissions where the results are essentially the same as represented in Figures 11-18.

(i) Similarly Example 2(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

fatty acid (oleic acid)	24 parts by volume;
water-insoluble alcohol (octanol)	8 parts by volume;
water-soluble alcohol (methanol)	24 parts by volume;
water	10 parts by volume; and
aqueous ammonia (28%)	3.8 parts by volume,

where the fuel additive ratio is about 65:35 to 50:50 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine and reduced noxious gases and remarkably reduced smoke and particulate emissions where the results are essentially the same as represented in Figures 11-18.

EXAMPLE 3

COMBUSTION TESTS WITH ADDITIVE COMPOSITION
(US ENVIRONMENTAL PROTECTION AGENCY FEDERAL TEST PROCEDURE
FOR STATIONARY SOURCES)

- 5 a) A confidential test experiment was performed at the Stockton East Water District, Stockton, California.

An independent emissions testing company, Normandean Associates of Berkeley, CA performed all emissions tests according to US Environmental Protection agency Federal Test Procedure for stationary sources. Additional particulate

- 10 measurements were taken to meet California Air Resource Board specifications.

The additive formulation for both test procedures was by parts, by volume:

32 parts linoleic acid

12 parts octanol

28 parts methanol

- 15 16 parts water

4.4 parts aqueous ammonia.

The engines were two Caterpillar V8 4-Stroke-Cycle Diesel engines (two of the four pumping engines at the site), number Engine # P27 and Engine # P28. Data for engine type and condition at time of testing are as follows:

- 20 # P273 Model: L2-2

Rated Horsepower: 319

Rated RPM: 1200

Total use hours: 38,761.1

OEM recommended use hours

- 25 before engine overhaul: 8,000.0

Use hours since last overhaul: 10,304.4

P28: Model: L2-2

Rated Horsepower: 319

- 30 Rated RPM: 1200

Total use hours: 31,001.0

OEM recommended use hours

before engine overhaul: 8,000.0

Use hours since last overhaul: 2,192.3

The test procedure observed was as follows:

- 5 At 10:30 a.m. on Day One of testing, Engine # P27 was stabilized at approximately 293 hp and exactly 1080 rpm while running on CA # 2 Diesel fuel. Three full emissions tests were run over the following consecutive four hours. See attached results in Table J as Column AA.

- 10 At 9:00 p.m. on Day One of testing, the fuel source for engine # P27 was switched to the above diesel: additive fuel blend. The engine ran from this fuel composition continuously until the end of testing on the following day.

At 10:00 a.m. on Day Two of testing engine # P27 was stabilized at approximately 293 hp and exactly 1078 rpm while running on the above mentioned diesel: additive fuel blend. Three full emissions tests were run over the following consecutive four hours. See attached results in Table J as Column BB.

- 15 At 10:30 a.m. on Day Three of testing, Engine # P28 was stabilized at approximately 319 hp and exactly 1200 rpm while running on CA # 2 Diesel fuel. Three full emissions tests were run over the following consecutive four hours in Table J as Column CC.

- 20 At 3:00 a.m. on Day Four of testing, the fuel source for engine # P28 was switched to the above diesel: additive fuel blend. The engine ran from this fuel composition continuously until the end of testing on the following day.

- 25 At 10:00 a.m. on Day Four of testing engine # P28 was stabilized at approximately 313 hp and exactly 1177 rpm while running on the above mentioned diesel: additive fuel blend. Three full emissions tests were run over the following consecutive four hours. See attached results in Table J as Column DD.

No mechanical changes were made to the engines during testing other than switching fuel source.

TABLE J
SUMMARY OF RESULTS

Test Parameters	AA	BB	CC	DD
	Engine P-27 Diesel Baseline	Engine P-27 66/35 Mix	Engine P-28 Diesel Baseline	Engine P-28 66/35 Mix
Gas Temperature, F	587	543	510	486
RPM	1,080	1,078	1,200	1,177
Average Flow Rate, dscfm	409	398	836	767
Moisture, %	9.8	11.3	6.9	8.2
Oxygen, dry %	6.1	6.1	11.8	12.8
Carbon dioxide, dry %	10.6	10.4	6.8	6.2
PARTICULATE MATTER (filters only)				
Concentration, gr/dscf	0.028	0.015	0.023	0.008
Emission Rate, lbs/hr	0.099	0.052	0.164	0.055
PARTICULATE MATTER (CARB)				
Concentration gr/dscf	0.056	0.037	0.041	0.021
Emission Rate, lbs/hr	0.197	0.126	0.294	0.139
OXIDES OF NITROGEN				
Concentration, ppmv	1208	1194	861	839
Emission Rate, lbs/hr as NO ₂	3.54	3.41	5.16	4.61
Concentration, Corrected to 15% O ₂	483	477	360	363
CARBON MONOXIDE				
Concentration, ppmv	1097	619	168	81
Emission Rate, lbs/hr	1.96	1.07	0.61	0.27
Concentration, Corrected to 15% O ₂	438	248	109	54
NON-METHANE HYDROCARBONS				
Concentration, ppmv as OI	5.3	10.1	8.5	9.9
Emission Rate, lbs/hr	0.004	0.007	0.013	0.014
Concentration, Corrected to 15% O ₂	2.1	4.0	5.5	6.6

Equations: Emission Rate, lb/hr = [Conc. ppm] x [Mol Wt] x [Flow Rate, dscfm] x 1.557E-7
Concentration, Corrected to 15% O₂ = [Conc. ppm] x [5.95/ (20.95-O₂ pct)]

These results represent the following significant toxic emissions improvements provided by the diesel: additive fuel composition compared to use of CA # 2 Diesel fuel:

	Engine *P27	Engine *P28
5 Particulates:		
gr/dscf	46% reduction	65% reduction
lbs/hr	47% reduction	66% reduction
Particulates (CARB):		
10 gr/dscf	33.9% reduction	48.8% reduction
lbs/hr	36% reduction	47% reduction
Oxides of Nitrogen:		
ppm	1.2% reduction	2.6% reduction
15 lbs/hr	3.7% reduction	11.7% reduction
Carbon Monoxide:		
ppm	44.6% reduction	51.8% reduction
lbs/hr	45.5% reduction	55.8% reduction

Non-Methane Hydrocarbon emissions were negligible for both Diesel fuel and the diesel: additive composition.

Fuel flow in engine # P27 increased from approximately 11 gal/hr to approximately 12 gal/hr, or an increase of 9%.

Fuel flow in engine # P28 increased from approximately 14 gal/hr to approximately 15 gal/hr, or an increase of 7%.

When allowance for variations in emissions flow rate, engine power, and fuel flow rate are evaluated, a slight timing change may be recommended for improved power.

EXAMPLE 4

a) A confidential test experiment was performed at California Truck Testing Services (CaTTS), a division of Clean Air Vehicle Technology Center (CAVTC), in

Hayward, CA.

CaTTS is located at the Chevron Research and Development Center in Richmond, CA. CaTTS test cell can accommodate vehicles as long as 65 feet. The centerpiece of the cell is a Froude-Consine direct-current electric chassis dynamometer, which consists of two 48-inch roll sets (with a distance from center to center of 53 inches).

The dynamometer tests both single-and tandem-axle vehicles with gross vehicle weight ratios of up to 85,000 pounds at a speed as high as 75 mph. The maximum power absorption at the roll is 500 horsepower. The dynamometer can simulate a wide variety of transient cycles.

The particulate emissions analysis system is a heated primary dilution tunnel, and a secondary tunnel for sample conditioning and particulate measurements.

The test vehicle was a 1984 MACK (Model WS767LT) single axle, Tractor VIN # WS7671T41238;

Differential: Rockwell R140 4,11:1

Tires: 285R75X24.5 retreads (40" diameter)

Transmission: Fuller RT 910

Engine: 10724613 Cummins NTC, CPL #393, Pump 9217

Rated: 400 hp@2100 rpm

Fuel Pressure: 172-194 psi

Engine flow rate: 139-145 lbs/hr

Injector flow rate: 193 mm/stroke

Intake manifold pressure: 31-39" Hg

Federal Certification Level: 10.6 grams/hp-hr NO_x

The transient test cycle was Code of Federal Regulations (CFR) §86.146-96 from CFR Volume 40 Part 86 (7-1-97 Edition).

This test cycle was a 16-minute urban transient cycle simulating urban conditions for a heavy-duty vehicle. The exact test cycle was repeated for the following fuels:

- 1) Standard CA # 2 Diesel Fuel
- 2) Fuel/Additive Composition #1
- 3) Fuel/Additive Composition #2

- 4) Fuel/Additive Composition #3
- 5) Fuel/Additive Composition #4
- 6) Standard CA #2 Diesel Fuel

The additive formulation for Fuel/Additive Composition #1 was, by parts, by

5 volume:

- | | |
|------------------------------|--------------------------------|
| 30 parts linoleic acid | (Henkel Emersol 315) |
| 10 parts ethoxylated alcohol | (Union Carbide Tergitol 1553) |
| 28 parts methanol | (Gallade Chemical, industrial) |
| 15 parts water | (Standard tap water) |
| 4.1 parts aqueous ammonia | (26% BAUM A) |

The additive formulation for Fuel/Additive Composition #2 was, by parts, by

volume:

- | | |
|-----------------------------|--------------------------------|
| 36 parts linoleic acid | (Henkel Emersol 315) |
| 6 parts ethoxylated alcohol | (Union Carbide Tergitol 1553) |
| 28 parts methanol | (Gallade Chemical, industrial) |
| 15 parts water | (standard tap water) |
| 4.1 parts aqueous ammonia | (26% BAUM A) |

The added formulation for Fuel/Additive Composition #3 was, by parts, by

volume:

- | | |
|-----------------------------|--------------------------------|
| 36 parts linoleic acid | (Henkel Emersol 315) |
| 6 parts ethoxylated alcohol | (Henkel Produce #33240) |
| 28 parts methanol | (Gallade Chemical, industrial) |
| 15 parts water | (standard tap water) |
| 4.1 parts aqueous ammonia | (26% BAUM A) |

The additive formulation for Fuel/Additive Composition #4 was, by parts, by

volume:

- | | |
|------------------------------|--------------------------------|
| 30 parts linoleic acid | (Henkel Emersol 315) |
| 10 parts ethoxylated alcohol | (Henkel Produce #3324)) |
| 28 parts methanol | (Gallade Chemical, industrial) |
| 15 parts water | (Standard tap water) |
| 4.1 parts aqueous ammonia | (26% BAUM A) |

A test cycle was run for each fuel in the order described above. A 10-minute

319

319

flushing cycle was run between each fuel sample. Clean filter samples were installed at the end of each test run. No changes were made to the truck, the engine, or the chassis dynamometer, except for the change in fuel source.

With reference to Figure 19, experimental results are described above in the

5 Brief Description of the Figures.

EXAMPLE 5

a) Similarly, Examples 3(a) or 4(a) are repeated except that the additive composition is replaced with the additive composition as follows:

Linoleic acid:oleic acid, 50:50	32 parts by volume
any C-8-10 alcohol;	12 parts by volume
ethanol denatured with methanol	
or iso-propanol;	28 parts by volume
water;	16 parts by volume
aqueous ammonia	4.4 parts by volume

15 Wherein the fuel/additive ratio is about 65:35 to 80:20 and the result of combustion of the resulting fuel additive composition compared to Diesel fuel is improved combustion, reduce carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions; where the results are essentially the same as represented in Examples 1(a), 2(a), 3(a) or 4(a).

20 b) Similarly, Examples 3(a) or 4(a) are repeated except that the additive composition is replaced with the additive composition as follows:

Linoleic acid:oleic acid, 50:50 (v/v)	32 parts by volume
any C-8-10 alcohol;	12 parts by volume
ethanol denatured with methanol	
or iso-propanol;	28 parts by volume
water;	8 parts by volume
aqueous ammonia	4.4 parts by volume

25 wherein the fuel/additive ratio is about 65:35 to 80:20 (v/v) and the result of combustion of the resulting fuel additive composition compared to Diesel fuel is
30 improved combustion, reduce carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions; and fuel efficiency is improved compared to 5(a).

c) Similarly, Examples 3(a) or 4(a) are repeated except that the additive composition is replaced with the additive composition as follows:

Linoleic acid:oleic acid, 50:50	16 parts by volume
any C-8-10 alcohol;	16 parts by volume
ethanol denatured with	
iso-propanol;	28 parts by volume
water;	4 parts by volume
aqueous ammonia	2.2 parts by volume

where the fuel/additive ratio is about 65:35 to 80:20 and the result of

10 combustion of the resulting fuel additive composition compared to Diesel fuel is improved combustion, reduced carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions; and improved storage characteristics compared to Example 5(b) and improved fuel consumption efficiency compared to Example 5(b).

15 d) Similarly, Examples 3(a) or 4(a) are repeated except that the additive composition is replaced with the additive composition as follows:

Linoleic acid:oleic acid, 50:50	16 parts by volume
any C-8-10 alcohol;	16 parts by volume
ethanol denatured with	
iso-propanol;	28 parts by volume
water;	4 parts by volume
aqueous urea (urea/water, 72/28,v/v)	4.4 parts by volume

20 where the fuel/additive ratio is about 80:20 to 95:5 and the result of combustion of the resulting fuel additive composition compared to Diesel fuel is improved
25 combustion, reduced carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions; and improved storage characteristics compared to Example 5(c)

e) Similarly, Examples 1(a), 2(a), 3(a) or 4(a) are repeated except that the additive composition is replaced with the additive composition as follows:

30 Linoleic acid:oleic acid, 50:50	8 parts by volume
any C-8-10 alcohol;	24 parts by volume
ethanol denatured with	

326

iso-propanol; 28 parts by volume
 water; 4 parts by volume
 aqueous ammonia 1.1 parts by volume

where the fuel/additive ratio is about 80:20 to 95:5 and the result of combustion

5 of the resulting fuel additive composition compared to Diesel fuel is improved combustion, reduced carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions; and improved storage characteristics compared to Example 5(d)

f) Similarly, Examples 1(a), 2(a), 3(a) or 4(a) are repeated except that the
 10 additive composition is replaced with the additive composition as follows:

ethoxylated alcohol 13S3 or 15S3 8 parts by volume
 any C-8-10 alcohol; 24 parts by volume
 ethanol denatured with
 iso-propanol; 28 parts by volume
 15 water; 4 parts by volume

where the fuel/additive ratio is about 80:20 to 95:5 and the result of combustion of the resulting fuel additive composition compared to Diesel fuel is improved combustion, reduced carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions; and improved storage

20 characteristics compared to Example 5(e).

g) Similarly, Examples 3(a) or 4(a) are repeated except that the additive composition is replaced with the additive composition as follows:

Any C8-10 alcohol; 28 parts by volume
 ethanol denatured with

25 iso-propanol; 28 parts by volume
 water; 1.5 parts by volume

where the fuel/additive ratio is about 90:10 to 95:5 and the result of combustion of the resulting fuel additive composition compared to Diesel fuel is improved combustion, reduced carbon buildup inside the engine; reduced smoke, particulates, and
 30 noxious gases; reduced unburnt hydrocarbon emissions; and improved storage characteristics compared to Example 5(e).

h) Similarly, Examples 3(a) or 4(a) are repeated except that the additive

composition is replaced with the additive composition as follows:

Any C8-10 alcohol; 28 parts by volume
 ethanol denatured with
 iso-propanol; 28 parts by volume

5 where the fuel/additive ratio is about 90:10 to 95:5 and the result of combustion of the resulting fuel additive composition compared to Diesel fuel is improved combustion, reduced carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions; and improved fuel storage characteristics compared to Diesel fuel and compared to Example 5(g).

EXAMPLE 6

a) Similarly, Examples 3(a) or 4(a) are repeated except that the additive composition is replaced with the additive composition as follows:

iso-propanol; 10 parts by volume
 ethanol 28 parts by volume

15 Where the engine is a spark-ignition engine and the fuel is gasoline, and where the fuel/additive ratio is about 90:10 to 95:5, and the result of combustion of the resulting fuel additive composition compared to gasoline is improved combustion, reduced carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions.

20 b) Similarly, Examples 3(a) or 4(a) are repeated except that the additive composition is replaced with the additive composition as follows:

any C-8-10 alcohol; 6 parts by volume
 ethanol denatured with
 iso-propanol; 28 parts by volume

25 where the engine is a spark-ignition engine and the fuel is gasoline, and where the fuel/additive ratio is about 90:10 to 95:5, and the result of combustion of the resulting fuel additive composition compared to gasoline is improved combustion, reduced carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions.

30 c) Similarly, Examples 3(a) or 4(a) are repeated except that the additive composition is replaced with the additive composition as follows:

ethoxylated alcohol 13S2 or 15S3; 2 parts by volume

ethanol denatured with

iso-propanol; 28 parts by volume

where the engine is a spark-ignition engine and the fuel is gasoline, and where the fuel/additive ratio is about 90:10 to 95:5, and the result of combustion of the resulting fuel additive composition compared to gasoline is improved combustion, reduced carbon buildup inside the engine; reduced smoke, particulates, and noxious gases; reduced unburnt hydrocarbon emissions.

EXAMPLE 7

(a) Similarly, Examples 1(a), 2(a), 3(a) are repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

Fatty acid (linoleic:oleic:myristic:palmitic:
stearic at ratios of 5:5:1:1:1) 44 parts by volume;
water-insoluble alcohol (hexanol:octanol:
decanol:oleyl:myristyl:palmityl at ratios
of 2:4:4:2:1:1) 22 parts by volume;
water-soluble alcohol (methanol:ethanol:
propanol:butanol at ratios of 2:4:2:1) 18 parts by volume;
water 6 parts by volume;
aqueous ammonia (28%) 6 parts by volume,

where the application is industrial or home furnaces and the fuel is heating oil or kerosene, and the fuel additive ratio is about 95:5 to 85:15 and the result of combustion of the resulting fuel/additive composition is reduced smoke, particulates, and noxious gases.

(b) Similarly, Examples 1(a), 2(a), 3(a) are repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

Fatty acid (linoleic:oleic:myristic:palmitic:
stearic at ratios of 5:5:1:1:1) 40 parts by volume;
water-insoluble alcohol (hexanol:octanol:
decanol:oleyl:myristyl:palmityl at ratios
of 2:4:4:2:1:1) 20 parts by volume;
water-soluble alcohol (methanol:ethanol:
propanol:butanol at ratios of 2:4:2:1) 16 parts by volume;

water 4 parts by volume;

aqueous ammonia (28%) 4 parts by volume,

where the application is industrial or home furnaces and the fuel is heating oil or kerosene, and the fuel additive ratio is about 95:5 to 85:15 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the furnace and further reduced smoke, particulates, and noxious gases.

(c) Similarly, Examples 1(a), 2(a), 3(a) are repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

Fatty acid (linoleic:oleic:myristic:palmitic:
tearic at ratios of 5:5:1:1:1) 36 parts by volume;
water-insoluble alcohol (hexanol:octanol:
decanol:oleyl:myristyl:palmityl at ratios
of 2:4:4:2:1:1) 18 parts by volume;
water-soluble alcohol (methanol:ethanol:
propanol:butanol at ratios of 2:4:2:1) 24 parts by volume;
water 12 parts by volume;
aqueous ammonia (28%) 4.9 parts by volume,

where the application is industrial or home furnaces and the fuel is heating oil or kerosene, and the fuel additive ratio is about 90:10 to 75:25 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the furnace and further reduced smoke, particulates, and noxious gases compared to compositions having a lower additive proportion.

(d) Similarly, Examples 1(a), 2(a), 3(a) are repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

Fatty acid (linoleic:oleic:myristic:palmitic:
tearic at ratios of 5:5:1:1:1) 34 parts by volume;
water-insoluble alcohol (hexanol:octanol:
decanol:oleyl:myristyl:palmityl at ratios
of 2:4:4:2:1:1) 16 parts by volume;
water-soluble alcohol (methanol:ethanol:
propanol:butanol at ratios of 2:4:2:1) 20 parts by volume;
water 9 parts by volume;

aqueous ammonia (28%) 4.6 parts by volume,

where the application is industrial or home furnaces and the fuel is heating oil or kerosene, and the fuel additive ratio is about 90:10 to 75:25 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the furnace and further reduced smoke, particulates, and noxious gases compared to compositions having a lower additive proportion..

(e) Similarly, Examples 1(a), 2(a), 3(a) are repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

- | | | |
|----|--|----------------------|
| 10 | Fatty acid (linoleic:oleic:myristic:palmitic:tearic at ratios of 5:5:1:1:1) | 32 parts by volume; |
| | water-insoluble alcohol (hexanol:octanol:decanol:oleyl:myristyl:palmityl at ratios of 2:4:4:2:1:1) | 16 parts by volume; |
| 15 | water-soluble alcohol (methanol:ethanol:propanol:butanol at ratios of 2:4:2:1) | 28 parts by volume; |
| | water | 15 parts by volume; |
| | aqueous ammonia (28%) | 4.9 parts by volume, |

where the application is industrial or home furnaces and the fuel is heating oil or kerosene, and the fuel additive ratio is about 80:20 to 65:35 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the engine and reduced noxious gases and remarkably reduced smoke and particulate emissions.

(f) Similarly, Examples 1(a), 2(a), 3(a) are repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

- | | | |
|----|--|---------------------|
| 25 | Fatty acid (linoleic:oleic:myristic:palmitic:tearic at ratios of 5:5:1:1:1) | 28 parts by volume; |
| | water-insoluble alcohol (hexanol:octanol:decanol:oleyl:myristyl:palmityl at ratios of 2:4:4:2:1:1) | 10 parts by volume; |
| 30 | water-soluble alcohol (methanol:ethanol:propanol:butanol at ratios of 2:4:2:1) | 24 parts by volume; |
| | water | 10 parts by volume; |

aqueous ammonia (28%) 3.8 parts by volume,

where the application is industrial or home furnaces and the fuel is heating oil or kerosene, and the fuel additive ratio is about 80:20 to 65:35 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the furnace and reduced noxious gases and remarkable reduced smoke and particulate emissions.

(g) Similarly, Examples 1(a), 2(a), 3(a) are repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

- | | | |
|----|--|----------------------|
| 10 | Fatty acid (linoleic:oleic:myristic:palmitic:tearic at ratios of 5:5:1:1:1) | 24 parts by volume; |
| | water-insoluble alcohol (hexanol:octanol:decanol:oleyl:myristyl:palmityl at ratios of 2:4:4:2:1:1) | 8 parts by volume; |
| 15 | water-soluble alcohol (methanol:ethanol:propanol:butanol at ratios of 2:4:2:1) | 24 parts by volume; |
| | water | 10 parts by volume; |
| | aqueous ammonia (28%) | 4.4 parts by volume, |

where the application is industrial or home furnaces and the fuel is heating oil or kerosene, and the fuel additive ratio is about 65:35 to 50:50 and the result of combustion of the resulting fuel/additive composition is improved combustion, reduced carbon buildup inside the furnace and reduced noxious gases and remarkably reduced smoke and particulate emissions.

DIAGNOSTIC SELECTION PROCESS—In another aspect, a diagnostic process was found which makes it possible for one of skill in the art to identify quickly components and quantities of an additive which when combined with a combustible fuel produces a clear stable micro-emulsion is needed in commercial application to improve combustion.

EXAMPLE A

DIAGNOSTIC TESTS WITH ADDITIVE COMPOSITIONS

a) Confidential test experiments were performed at 534 Ashbury Street, San Francisco, CA.

5 The glassware used were standard glass and pyrex beaker, graduated cylinders, pipettes, erlenmeyer flasks and 4 oz. boston round bottles purchased from VWR Scientific Products in San Francisco, CA and from Bryant Laboratory, Inc. in Berkeley, CA.

The beakers were of the general description PYREX brand Double Scale Griffin Beakers, graduated, 30, 50, 100 and 250 ml capacity Corning Nos. 1000-30, 1000-50, 10 1000-100 and 1000-250.

The graduated cylinders were of the general description Graduated Cylinders Single metric Scale White line, 10, 25, and 50 ml capacity with milliliter divisions of 0.2, 0.5, and 1.0 respectively.

The pipettes were of the general description KIMAX-51 Measuring (Mohr)

15 Pipets, reusable, Class B, Color-Coded, SAFE-Gard tempered tip, intended for chemical laboratory work, 1 ml and 5 ml capacity.

The Erlenmeyer flasks were of the general description PYREX brand, Erlenmeyer, Narrow Mouth, Graduated Flask, 100 ml and 250 ml capacity.

20 The Boston round bottles were of the general description Boston Round Bottles, Narrow Mouth, Qorpak, with Polyseal-lined black phenolic caps, 120 ml (4 oz) capacity.

Chemical components used in the following experiments were generally supplied as samples by chemical companies such as Henkel Corporation, of Cincinnati, OH; and Union Carbide, of Chicago, IL; or as generally-sold products from Gallade

25 Chemical, Inc. of Newark, CA; VWR Scientific of San Francisco, CA; and Bryant Laboratory, Inc. of Berkeley, CA.

All laboratory equipment was used exactly as shipped from the above mentioned suppliers; and all chemical components were used exactly as shipped from the above mentioned suppliers, with no further purification or other alterations.

30 CA #2 Diesel fuel was purchased from standard public Diesel fuel distributors in San Francisco, from standard gas station pumps.

Where the following components were added in the following order to a 250 ml

Erlenmeyer flask:

34 ml linoleic acid (Henkel Corporation product Emersol 305)

6 ml octanol (Henkel Corporation product # 3324)

28 ml methanol (Gallade Chemical, Inc. technical grade)

5 gentle swirling produced Freuhoffer lines and then a clear solution, to which was added:

14.6 ml water (standard tap water)

gentle swirling produced a white, milky solution, to which was added, by pipette:

4.6 ml aqueous ammonia (Gallade Chemical, Inc. Baum A 26%)

an immediate exothermic reaction took place, producing mild heat and immediate

10 visual change of the solution from milky to clearing; where gentle swirling produced complete clearing of the mixture.

A 120 ml (4 oz) boston bottle was then partially filled with

80 mls diesel fuel (CA standard #2 Diesel fuel)

to which was added:

15 20 ml of the above clear fatty acid/alcohol/water/ammonia composition; gentle swirling produced a clear, microemulsion composition that remained stable over time after 6 months the microemulsion is still clear, and stable although fatty acid degradation has caused a color change from no color to light amber color).

20 This 100 ml microemulsion sample was then stored overnight at 20°C in a standard home freezing unit, where freezer temperature was measured using a standard freezer thermometer such as can be purchased in a hardware store.

On immediate removal from the freezing unit, the microemulsion composition showed partial 'slushy' solidification, similar or identical to solidification of 100 ml of 100% Diesel fuel stored simultaneously in the same freezing unit.

25 After ten minutes, the microemulsion composition and the 100% Diesel fuel thawed entirely, returning to a clear, liquid state. The microemulsion composition showed no visible signs of phase separation.

b) Similarly, Example A(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

30	50/50 linoleic acid/oleic	32	parts by volume
	C8-10 alcohol;	16	parts by volume
	methanol;	28	parts by volume

75

water; 12 parts by volume
aqueous ammonia 3.3 parts by volume

where the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces an exothermic reaction, and a clear microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C, where fatty acids will show discoloration and other signs of oxidation over time.

c) Similarly, Example A(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

10 50/50 linoleic acid/oleic 24 parts by volume
C8-10 alcohol; 16 parts by volume
methanol; 28 parts by volume
water; 8 parts by volume
aqueous ammonia 3.3 parts by volume

15 where the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces an exothermic reaction, and a clear microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C, where the fuel/additive composition will show discoloration or other signs of oxidation from fatty acids over time compared to

20 Examples A(a) and A(b).

d) Similarly, Example A(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

25 50/50 linoleic acid/oleic 16 parts by volume
C8-10 alcohol; 16 parts by volume
ethanol denatured with methanol; 28 parts by volume
water; 4 parts by volume
aqueous ammonia 2.2 parts by volume

where the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces an exothermic reaction, and a clear microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C, where the fuel/additive composition will show significantly less discoloration or other signs of oxidation from fatty acids over time

76

compared to Examples A(a), A(b) and A(c).

e) Similarly, Example A(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

5 50/50 linoleic acid/oleic 16 parts by volume
C8-10 alcohol; 16 parts by volume
ethanol denatured with methanol; 28 parts by volume
water; 4 parts by volume
aqueous urea 4.4 parts by volume

where the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces an exothermic reaction, and a clear microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C, and the nitrogen content of the fuel/additive composition is increased compared to Example A(d).

f) Similarly, Example A(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

15 50/50 linoleic acid/oleic 8 parts by volume
ethoxylated alcohols 13S3 or 15S3 8 parts by volume
C8-10 alcohol; 16 parts by volume
ethanol denatured with methanol; 28 parts by volume
20 water; 4 parts by volume
aqueous ammonia 2.2 parts by volume

where the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces an exothermic reaction, and a clear microemulsion composition that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C, where fuel/additive composition will show further reduction of discoloration and other signs of oxidation from fatty acids over time compared to Examples A(a), A(b), A(c), A(e) and A(d).

g) Similarly, Example A(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

30 ethoxylated alcohols 13S3 or 15S3 16 parts by volume
C8-10 alcohol; 16 parts by volume
ethanol denatured with methanol; 28 parts by volume

water; 4 parts by volume

where the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear microemulsion composition (with no discernable exothermic reaction) that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C, where no discoloration or other signs of oxidation occur over time.

h) Similarly, Example A(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

C8-10 alcohol; 32 parts by volume

ethanol denatured with iso-propanol; 28 parts by volume

water; 2 parts by volume

where the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear microemulsion composition (with no discernable exothermic reaction) that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C, where no discoloration or other signs of oxidation occur over time and no ethylene oxides are present in the fuel/additive.

i) Similarly, Example A(a) is repeated except that the additive composition and amounts are replaced to be the additive composition as follows:

C8-10 alcohol; 24 parts by volume

anhydrous ethanol

denatured with iso-propanol; 28 parts by volume

where the fuel/additive ratio is about 65:35 to 95:5 and the result of mixing by gentle swirling produces a clear microemulsion composition (with no discernable exothermic reaction) that remains stable over time, up to 6 months or longer, and during and after storage at a temperature of -20°C, where no discoloration or other signs of oxidation occur over time and no ethylene oxides are present in the fuel/additive.

EXAMPLE B

DETERMINING SURFACE ACTIVITY STRENGTH OF VARIOUS WATER-INSOLUBLE ALCOHOLS

Experiments # 1,2,3, & 4 all begin with 32 mls anhydrous ethanol to which is

added 32 mls of the following alcohols:

1 98% pure C8 alcohol (straight chain)

2 combination C8 and C10 alcohols (straight chain)

3 combination C6 through 12 alcohols (straight chain)

4 2-ethyl-hexanol-1 (branched chain)

Alcohols 1,2,3 and 4 mixed readily with ethanol, but for all of them, mixing is not considered complete until Freuhoffer lines disappear. This happens with very gentle swirling of the beaker or stirring.

80 mls of CA # 2 Diesel fuel was then poured into four separate clean beakers and 20 mls of each of the above ethanol/water-insoluble alcohol combinations were added, one mixture to each beaker.

1 C8 alcohol was hazy at first, but after gentle "sloshing" or swirling, the mixture was perfectly clear.

Hundreds of previous experiments have proven that once the mixture has gone clear, it is stable and will remain stable at temperatures of -20°C or lower.

Therefore, 98% pure, straight-chain C8 alcohol, can be used by itself as the only necessary surfactant when introducing anhydrous ethanol into Diesel fuel.

2 The C8-10 alcohol combination was hazy at first, but cleared almost immediately with the slightest agitation. There was a quality of instantaneous clearing that the C8 alcohols lacked, but was quite evident in this experiment.

Previous experiments have shown that this instant clearing quality indicates superior surface activity. This superior performance manifests not so much in a 'more stable solution' (once the solution is clear, it is stable), but that the superior solution will tolerate components that are more hydrophilic than anhydrous ethanol (i.e. methanol, water) and still remain stable.

Therefore, the combination straight-chain C8-10 can be used by itself as the only necessary surfactant when introducing anhydrous ethanol into Diesel fuel and is a superior surfactant to 98% pure C8 alcohol.

3 The C6-12 alcohol combination was completely hazy at first, meaning that there was an opaque quality to the solution rather than a more pearly quality evident in the previous two experiments.

This opaque quality usually signifies that there is 'a long way to go' before the surface activity is strong enough to produce a clear solution. Swirling, sloshing, shaking did nothing to promote clearing.

Previous experiments have shown that if a solution does not clear, it will eventually show phase separation, sometimes slowly at room temperature, but very quickly at lower temperatures.

Therefore, the combination straight-chain C6-12 alcohol cannot be used by itself as the only necessary surfactant when introducing anhydrous ethanol into Diesel fuel. By inference, it is also true that C6-12 alcohols will not tolerate components that are more hydrophilic than anhydrous ethanol.

4 The branched chain 2-ethyl-1-hexanol solution was hazy at first, but possessed the pearly quality observed in experiments 1 and 2. Swirling did not produce immediate clearing, but over time (4 minutes) the solution cleared on its own with no further agitation. Swirling produced a slightly hazy quality again, but standing for one more minute, the solution became perfectly clear and remained clear.

Previous experiments have shown that this 'delay' quality indicates relatively weak surface activity compared to components that produce immediately clear results. This inferior performance manifests not so much in a 'less stable solution' (once the solution is clear, it is stable), but that the inferior solution will not tolerate components that are more hydrophilic than anhydrous ethanol, but will benefit from higher concentrations of the surface active component.

Therefore, the branched chain 2-ethyl-hexanol-1 can be used by itself as the only necessary surfactant when introducing anhydrous ethanol into Diesel fuel, but is not as strong a surfactant as either the C8 alcohol or the C8-10 alcohols combination.

REDUCE OCTANOL SERIES USING C8, C8-10, C6-12 and 2EH-1

# 1	# 2	# 3	# 4
37. Ethanol	32. Ethanol	32. Ethanol	32. Ethanol
32. Henkel 3324	32. Henkel 3328	32. Henkel 3393	32. Baker
C8 Alcohol	C8-10 Alcohol	C6-12 Alcohol	2EH1
80 ml Diesel	80 ml Diesel	80 ml Diesel	80 ml Diesel
20 ml # 1	20 ml # 2	20 ml # 3	20 ml # 4
Hazy at first	Hazy at first	Completely hazy	Hazy
Shaking	Clearing	Sloshing, Shaking	But almost
Perfectly clear	Almost immediately	No change	Clearing
---	Gentle slosh	Stays hazy	Perfectly
---	Instant Clear	---	Over time
---	---	---	(4 min)
---	---	5 minutes	CLEAR!
---	---	Enter Pearly	SLIGHTLY PERSISTENT

NEXT SERIES: Beakers have the following amounts remaining in them:

# 1A	# 2A	# 3A	# 4A
22. Ethanol	22. Ethanol	22. Ethanol	22. Ethanol
22. Henkel 3324	22. Henkel 3328	22. Henkel 3393	22. Baker
C8 Alcohol	C8-10 Alcohol	C6-12 Alcohol	2EH1
Add 7 ethanol	Add 7 ethanol	Add 7 of C6-12 alcohol	Add 7 ml 2EH1
80 ml Diesel	80 ml Diesel	80 ml Diesel	80 ml Diesel
20 ml # 1A	20 ml # 2A	20 ml # 3A	20 ml # 4A
Hazy, period	Hazy, period	Hazy	Clear immediately

EXAMPLE C

VERIFICATION OF SUPERIOR SURFACE ACTIVITY OF
LINOLEIC ACID WITH AMMONIA

Experiments # 1 and # 2 both begin with 32 mls 5% aqueous ethanol to which is

5 added:

- # 1 28 mls C8-10 alcohol
4 mls linoleic acid
5 mls aqueous ammonia (28% ammonia/72% water)

10 # 2 32 mls C8-10

Note that, as closely as possible, the ethanol: total surfactant ratio is 1:1 for both experiments.

1

Aqueous ethanol and C8-10 alcohol mix fairly readily, where Freuhoffer lines are visible until mixing is complete.

15

The addition of linoleic acid produced a milky solution.

The addition of aqueous ammonia produces instant clearing and heat.

When 20 mls of this mixture is added to 80mls of CA #2 Diesel Freuhoffer lines are evident (Freuhoffer lines are not the same as 'haze', but are clear,

20

oily, lines that resemble smoke wisps). Then the mixture goes perfectly clear, signifying as mentioned above, that the composition is stable.

Previous experiments have shown that linoleic acid and ammonia, together, are a potent (antonic) surfactant that can be depended on to produce stable micro-emulsions, even in the presence of large quantities of very hydrophilic components, namely, methanol and water.

25

#2

Aqueous ethanol and C8-10 alcohol mixed readily as above.

When 20 mls of this mixture is added to 80mls of CA#2 Diesel the composition exhibits a very fine haze first, and then clears.

30

However, previous experiments have shown that the initial haze signifies weaker surface activity than in the experiment where linoleic acid with ammonia did not exhibit any hazy quality when mixed with Diesel fuel.

EXAMPLE D

VERIFICATION OF SUPERIOR SURFACE ACTIVITY OF
C8-10 ALCOHOL COMBINATION OVER 2EH-1

Experiments #1 and #2 both begin with 32 mis anhydrous methanol to which is

5 added:

- #1 32 mls C8-10 alcohol combination
#2 32 mls 2 ethyl hexanol 1

Alcohols 1 and 2 mixed readily with the methanol, but mixing is not considered complete until Freuhoffer lines disappear. This happens with very gentle swirling of

10 the beaker or stirring.

80 mls of CA #2 Diesel fuel was then poured into each of two separate clean beakers and 20 mls of each of the above alcohol combinations were added respectively, one mixture to each beaker.

#1

15 The C8-10 alcohol mixture was pearly, hazy at first. It was almost clear, but there is a definite moment when a mixture becomes really clear. It is only then that the mixture can be considered stable.

After 4 minutes, with gentle swirling, the haze had diminished significantly, but not until 5 minutes later that the solution became completely clear.

20

Therefore, while C8-10 alcohol can be used by itself as the only necessary surfactant when introducing anhydrous methanol into Diesel fuel, it is not ideal for this application, and would benefit from the presence of a stronger surfactant, such as linoleic with ammonia, as described above.

25 #2

2-ethyl hexanol-1 was cloudy (not hazy) at first, meaning opaque and definitely not leaning toward clearing. Swirling, sloshing, stirring did nothing to promote clearing.

Therefore, 2FH-1 alcohol cannot be used by itself in this ratio as the only necessary surfactant when introducing anhydrous methanol into Diesel fuel and is proven to be a weaker surfactant than the C8-10 combination.

30

EXAMPLE E

BENEFIT OF INCREASING SURFACE ACTIVE COMPONENT
WHEN USING RELATIVELY WEAK SURFACTANT

#2A

5 5 additional mls of 2-ethylhexanol-1 (2EH-1) were added to the remaining
#2 alcohol mixture, above, producing a methanol 22.27 2EH-1 mixture.
20 mls of this mixture was then added to a beaker with 80ml of CA Diesel
fuel.

10 The mixture went clear immediately, illustrating that comparatively weak
surfactants benefit from an increase in the ration of surfactant to water
soluble alcohol.

The many Examples described herein above may use water as a component. It is
to be understood in the many examples that when the water content is reduced by half, by
quarter or by 90%, equal or better results in combustion improvement are obtained.

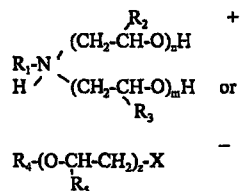
15 While only a few embodiments of the invention have been shown and described
herein, it will become apparent to those skilled in the art that various modifications and
changes can be made in the present invention to the present additive composition to
produce fuel/additive microemulsions with a combustible fuel, without departing from the
spirit and scope of the present invention. All such modification and changes coming
20 within the scope of the appended claims are intended to be carried out thereby.

I CLAIM:

1. An additive composition for a combustible fuel, which is also used as a
fuel composition, to utilize readily available and renewable resources, to improve liquid
combustible fuel properties, reduce undesirable elements such as sulphur, aromatic
5 hydrocarbons, and glycerine from the content of the fuel, produce improved
combustion, and to reduce visible smoke, particulates and other noxious emissions
production of the combusted fuel, which additive or fuel composition comprises:
 - a. one or more alcohols selected from the group consisting of water-soluble
alcohols:
 - 10 (i) having between about 1 and 2 carbon atoms, selected from the group
consisting of methanol and ethanol in an anhydrous state or as a 0.5-36% aqueous
solution by volume; or
 - (ii) having between about 3 and 5 carbon atoms, selected from the group
consisting of propanol, iso-propanol, butanol, and pentanol by volume or combinations
 - 15 of (a)(i) and a(ii); and
optionally one or more of the following:
 - b. one or more alcohols selected from the group consisting of:
 - (i) straight or branched chain, saturated or unsaturated alcohols, which are
clear and liquid at room temperature, and having between about 6 and 12 carbon atoms,
 - 20 or
 - (ii) straight- or branched-chain, saturated or unsaturated long-chain fatty
alcohols, which are solid at room temperature, having from between about 13 and 18
carbon atoms, or combinations of (b)(i) and (b)(ii);
 - c. one or more ethoxylated alcohols selected from the group consisting of
 - 25 alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is
less than 5 moles (units);
 - d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from
alkyl, alkenyl or alkynyl having between about 10 to 24 carbon atoms, with
 - e. a source of nitrogen in an anhydrous state or as an aqueous solution
 - 30 selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl
hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine
wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl,
wherein trialkylamines are excluded;

wherein components a and one or more of b, c, d, and e, when combined with mixing with combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 0:100 by volume;

wherein said additive/fuel composition excludes ethylene glycol, glycerine, polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general formula:



wherein R₁ and R₄ each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 carbon atoms (e.g., alkyl or alkenyl) or R₄ is alkylphenyl of 1 to 18 carbon atoms in the optionally branched alkyl chain or H; R₂, R₃ and R₅ each independently represent a methyl group or H, n plus m is an integer from 1 to 20; z is an integer from 0 to 15; and X is -COO(-) or -OCH₂COO(-), wherein, substituents R₂, R₃ and R₅ are the same or different in different monomer units of each chain, and optionally other organic diacids are excluded.

2. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 2 carbon atoms as defined herein in (a)(i), in an anhydrous state or as a 0.5-10% aqueous solution; and

b. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 3 and 5 carbon atoms as defined herein in (a)(ii),

wherein components a and b, when combined with mixing with the refined combustible fuel, form a clear stable solution or microemulsion having a viscosity

similar to that of the liquid combustible fuel and where the ratio of combustible fuel:

additive ranges from about 99:1 to 1:99 by volume.

3. The additive composition of claim 1 wherein:

a) one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 2 carbon atoms as defined herein in a(i) in an anhydrous state or as a 0.5-5% aqueous solution;

b) one or more alcohols selected from the group consisting of alcohols, iso-propanol and butanol;

wherein components a and b, are present in a:b ratios from about 80:20 and 99:1 by volume wherein components a and b, when combined with mixing with the liquid combustible fuel, form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 90:10 to 95:5 by volume.

4. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution;

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain, alcohols having between about 6 and 12 carbon atoms,

wherein components a and b, are present in a:b ratios ranging from about 3:1 and 1:3, wherein components a and b, when combined with mixing with combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 by volume.

5. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 5% aqueous solution denatured with iso-propanol, butanol or combinations thereof;

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 12 carbon atoms;

wherein components a and b, are present in a:b ratios ranging from 3:1 and 1:1 by volume wherein components a and b, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges

5 from about 80:20 to 99:1 by volume.

6. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein, in an anhydrous state or as a 0.5-20% aqueous solution; and

10 b. one or more alcohols selected from the group consisting clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms; and

c. one or more alcohols selected from the group consisting of ethoxylated alcohols having between about 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

wherein components a, b, and c are present in a:b:c ratios ranging from about 4:1:1 and 1:4:4 by volume, wherein components a, b, and c when combined with mixing with the combustible fuel, form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel:

20 additive ranges from about 99:1 to 1:99 by volume.

7. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution;

25 b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 12 carbon atoms;

c. one or more alcohols selected from the group consisting of ethoxylated alcohols having between about 12 and 16 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

wherein components a, b, and c are present in a:b:c ratios ranging from about 4:1:1 and 1:4:4 by volume, and more preferably between about 4:1:1 and 4:2:1 by volume wherein components a, b, and c when combined with mixing with combustible

fuel, form a clear, stable microemulsion having a viscosity similar to that of the liquid fossil fuel, and where the ratio of combustible fuel: additive ranges from between about 80:20 and 99:1 by volume.

8. The additive composition of claim 1 wherein:

5 a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5 to 20% aqueous solution; and

b. one or more alcohols selected from the group consisting of alcohols having between about 6 and 18 carbon atoms, ethoxylated where the ethylene oxide add-on is less than 5 moles;

10 wherein components a and b are present in a:b ratios ranging from between 3:1 and 1:2 by volume, wherein components a and b when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 by volume.

9. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution or combinations thereof;

20 b. one or more alcohols selected from the group consisting of alcohols having between about 6 and 12 carbon atoms ethoxylated where the ethylene oxide add-on 3 moles;

wherein components a and b are present in a:b ratios ranging from 3:1 and 1:2 by volume, and more preferably between about 3:1 and 2:1 by volume, wherein components a and b when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 65:35 to 99:1.

10. The additive composition of Claim 1 wherein:

30 a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution or combinations thereof;

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between

331

about 6 and 12 carbon atoms, and

c. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms;

d. a source of nitrogen in an anhydrous state or as an aqueous solution

5 selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or iso-propyl, wherein trialkylamines are excluded; sufficient to neutralize between about 40 to 85 percent of the fatty acid of subpart c;

10 wherein components a, b, and c are present in a:b:c ratios ranging from about 4:1:1 and 1:4:4; by volume, wherein components a, b, c and d when combined with mixing with said combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 80:20 and 99:1 by volume.

15 11. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and

20 b. one or more alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, ethoxylated where the ethylene oxide add-on is 3 moles; and

c. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms; and

25 d. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded,

30 wherein components a, b, and c are present in a:b:c ratios ranging from about 5:1:1 and 1:4:4 by volume; wherein components a, b, c, and d when combined with mixing with the combustible fuel, form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 99:1 to 1:99 by volume.

12. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-20% aqueous solution or combinations thereof;

5 b. one or more alcohols selected from the group consisting of ethoxylated alcohols having between about 12 and 16 carbon atoms, where the ethylene oxide add-on is 3 moles;

c. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms;

10 d. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded, sufficient to neutralize between about 40 to 85 percent of the fatty acid of subpart c;

15 wherein components a, b, and c are present in a:b:c ratios ranging from about 4:1:1 and 1:4:4; and preferably between about 4:1:1 and 3:1:1 by volume, wherein components a, b, c, and d when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 80:20 to 99:1 by volume.

13. The additive composition of Claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and

25 b. one or more alcohols selected from the group consisting of saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms; and

30 c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles; and

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms; and

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine, wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl,

5 wherein trialkylamines are excluded;

wherein components a, b, c, and d are present in a:b:c:d ratios ranging from about 6:1:1:1 and 1:4:4:4 by volume; wherein components a, b, c, d, and e when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of

10 combustible fuel: additive ranges from about 99:1 to 1:99 by volume.

14. The additive composition of Claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein, in an anhydrous state or 5 to 10% aqueous ethanol denatured with methanol, iso-propanol, butanol or

15 combinations thereof;

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 12 carbon atoms;

c. one or more alcohols selected from the group consisting of ethoxylated

20 alcohols having between about 12 and 16 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atom; and preferably oleic acid and linoleic acid;

25 e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded. sufficient to neutralize between about 40 to 85

30 percent of the fatty acid of subpart c;

wherein components a, b, c, and d are present in a:b:c:d ratios ranging from about 6:1:1:1 and 1:4:4:4 by volume, wherein components a, b, c, d, and e when combined with mixing with the combustible fuel form a clear, stable microemulsion

having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 80:20 to 99:1 by volume.

15. The additive composition of Claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble

5 alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of

10 alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms with

15 e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

20 wherein components a and one or more of b, c, d, and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 95:5 to 99:1 by volume.

16. The additive composition of claim 1 wherein:

25 a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between

30 about 6 and 18 carbon atoms, or between about 6 and 12 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein components a and one or more of b, c, d, and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 90:10 to 99:1 by volume.

17. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution, and one or more of the following:

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded;

wherein components a and one or more of b, c, d and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 80:20 to 99:1 by volume.

18. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded;

wherein components a and one or more of b, c, d and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to that of the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 60:40 to 99:1 by volume.

19. The additive composition of Claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution

selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

- 5 wherein components a and one or more of b, c, d, and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 50:50 to 99:1 by volume.

20. The additive composition of Claim 1 wherein:

- 10 a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

- b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between
15 about 6 and 18 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

- d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from
20 alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl

- 25 wherein trialkylamines are excluded;

wherein components a and one or more of b, c, d and e, when combined with mixing with the combustible fuel form a clear, stable microemulsion having a viscosity similar to the liquid combustible fuel, and where the ratio of combustible fuel: additive ranges from about 1:99 to 50:50 by volume.

- 30 21. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms;

- c. one or more ethoxylated alcohols selected from the group consisting of
5 alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

- e. a source of nitrogen in an anhydrous state or as an aqueous solution
10 selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl wherein trialkylamines are excluded;

wherein the combustible fuel is any conventional or synthetic combustible fuel.

- 15 22. The additive composition of claim 1, wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

- b. one or more alcohols selected from the group consisting of clear, liquid
20 saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is less than 5 moles;

- 25 d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

- e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine
30 wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein the combustible fuel is a fossil fuel such oil, jet fuel, kerosene, other distillate fuels, coal as Diesel fuel, heating slurry, gasoline or combinations thereof.

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23. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

5 b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is

10 less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl

15 hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein the combustible fuel is a renewable oil, such as triglycerides from any feedstock, esterification products, waste vegetable oils, tallow, tall oils or combinations

20 thereof.

24. The additive composition of claim 1 wherein:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

25 b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is

30 less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution

selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl, ethyl, n-propyl or isopropyl, wherein trialkylamines are excluded;

5 wherein the combustible fuel is other alcohols, such as long-chain saturated fatty alcohols which are solid at room (ambient) temperature, having between about 12 and 18 carbon atoms.

25. An additive composition for a combustible fuel, which may also be used itself as a fuel composition, to utilize readily available and renewable resources and produce improved fuel performance and combustion, which fuel comprises a composition of components:

a. one or more alcohols selected from the group consisting of water-soluble alcohols having between about 1 and 5 carbon atoms as defined herein in an anhydrous state or as a 0.5-36% aqueous solution; and one or more of the following:

15 b. one or more alcohols selected from the group consisting of clear, liquid saturated or unsaturated, straight- or branched-chain alcohols having from between about 6 and 18 carbon atoms;

c. one or more ethoxylated alcohols selected from the group consisting of alcohols having between 6 and 18 carbon atoms, where the ethylene oxide add-on is

20 less than 5 moles;

d. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms, with

e. a source of nitrogen in an anhydrous state or as an aqueous solution selected from the group consisting of the ammonia, hydrazine, alkyl hydrazine, dialkyl

25 hydrazine, urea, ethanolamine, monoalkyl ethanolamine, and dialkyl ethanolamine wherein alkyl is independently selected from methyl ethyl n-propyl or isopropyl, wherein trialkylamines are excluded;

wherein the above composition comprises the total combustible fuel and the ratio of the other combustible fuels: above composition is 0:100.

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26. An additive composition for a combustible fuel to produce improved combustion and reduced smoke and particulate production of the fuel, which additive comprises a composition of components:

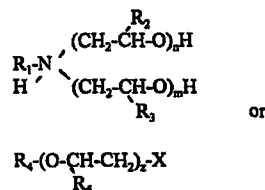
a. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms is present in between about 15 and 60 parts by volume;

b. at least one alcohol selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol and clear liquid alcohols having from between about 6 and 12 carbon atoms, is present in between about 18 and 75 parts by volume, where methanol is combined with at least one other alcohol;

c. water which is present in between about 2 and 32 parts by volume; and

d. urea sufficient to neutralize between about 40 to 70 percent of the fatty acid of subpart a;

wherein the additive composition optionally excludes ethylene glycol, glycerine, polyethylene, polypropylene, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general formula:



wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or R_4 is alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or H; R_2 , R_3 and R_3 each independently represent a methyl group or H, n plus m is a number from 1 to 20; z is a number from 0 to 15; and X is $-COO(-)$ or $-OCH_2COO(-)$, wherein, substituents R_2 , R_3 and R_3 the same or different in different monomer units of each chain, and optionally other organic diacids are excluded.

Preferably the fuel/additive is in a ratio to produce a water-in-oil (w/o) emulsion, i.e., between about 50:50 to 95:5, more preferably between about 65:35 to 90:10, and most preferably about 80:20 to 85:15.

27. An additive composition for a combustible fuel to produce improved combustion and reduced smoke and particulate production of the fuel, which additive

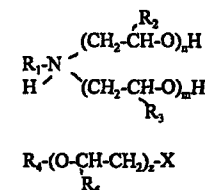
comprises a composition of components:

a. a fatty acid of the structure $R-(C=O)-OH$, wherein R is selected from alkyl, alkenyl or alkynyl having from about 10 to 24 carbon atoms is present in between about 15 and 60 parts by volume;

b. ethanol is present in between about 18 and 75 parts;

c. water which is present in between about 2 and 32 parts by volume; and
d. urea and/or ammonia sufficient to neutralize between about 40 to 70 percent of the fatty acid of subpart a;

wherein the additive composition optionally excludes ethylene glycol, glycerine, polyethylene, polyoxyethylene, polyoxypropylenes, aromatic organic compounds, sulfur, sulfur compounds, metals, metal compounds, compounds of phenanthrene, and emulsifiers of the general formula:



wherein R_1 and R_4 each independently is a saturated or unsaturated, straight-chain or branched hydrocarbon aliphatic radical each of 4 to 24 C atoms (e.g., alkyl or alkenyl) or R_4 is also can be alkylphenyl of 1 to 18 C atoms in the optionally branched alkyl chain or H; R_2 , R_3 and R_3 each independently represent a methyl group or H, n plus m is to be a number from 1 to 20; z can be a number from 0 to 15; and X is $-COO(-)$ or $-OCH_2COO(-)$, wherein, substituents R_2 , R_3 and R_3 are the same or different in different monomer units of each chain, and optionally other organic diacids are excluded, wherein the fuel/additive is a ratio to produce a water-in-oil (w/o) emulsion, between about 65:35 to 90:10 by volume.

28. The addition of claim 1 which is selected from the group consisting of:

- a) fatty acid (linoleic/oleic (50:50) 24 parts by volume
C8-10 alcohol (2 EH-1) 8 parts by volume
5% aqueous ethanol, denatured

with methanol 32 parts by volume
ammonia 3.3 parts by volume

where the additive: fossil fuel ratio is 10:90 to 5:95; or

- b) fatty acid (linoleic/oleic (50:50) 16 parts by volume
C8-10 alcohol (2 EH-1) 16 parts by volume

5% aqueous ethanol, denatured 32 parts by volume
with methanol 2.2 parts by volume
ammonia

where the additive: fossil fuel ratio is 10:90 to 5:95

29. A method to determine the suitability of a composition as a useful

additive to a combustible fuel to improve combustion, which method comprises:

- a. combining first a fatty acid at ambient conditions with water in soluble alcohol;
- b. adding water soluble alcohol, water or combinations thereof; observing a cloudy mixture when water is added;
- c. adding aqueous ammonia with low shear agitation with the production of mild heat of reaction and observing clearing of the mixture forming an emulsion; and
- d. adding the clear mixture of step (c) to diesel fuel observing a clear mixture of addition with (diesel fuel, with the proviso that if clearing doesn't occur in both step (c) and step (d) then the microemulsion formed by the additive/diesel fuel will not be stable and will separate over time or at temperature below 0°C.

Fig. _1



Fig. _2

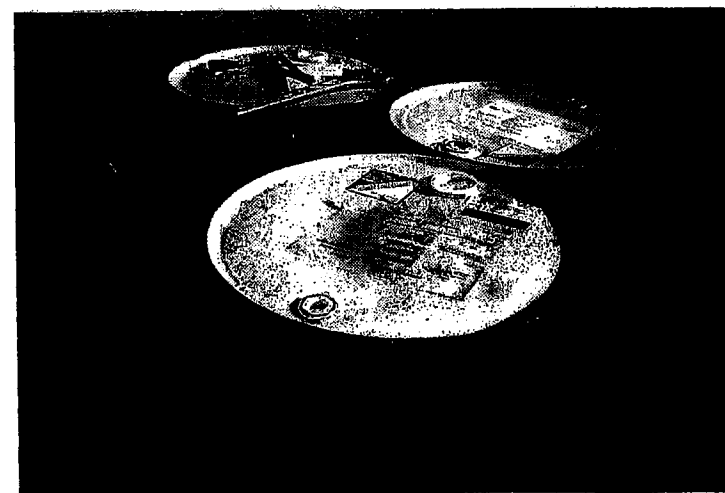


Fig. _3

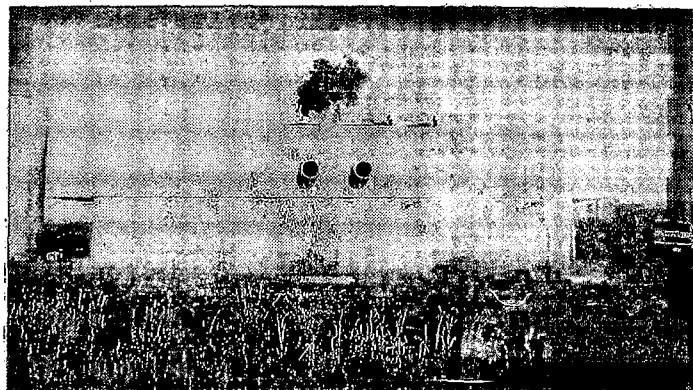


Fig. _4

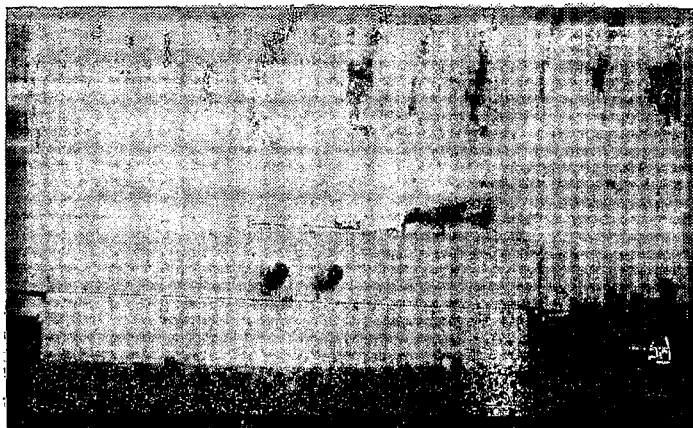


Fig. _5

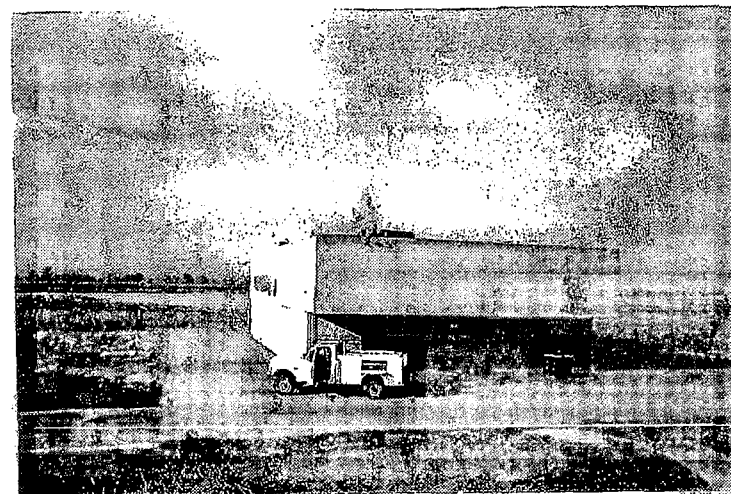
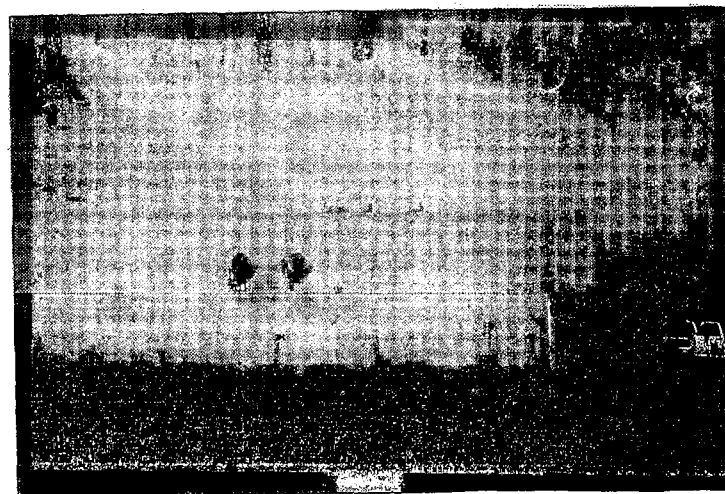


Fig. _6

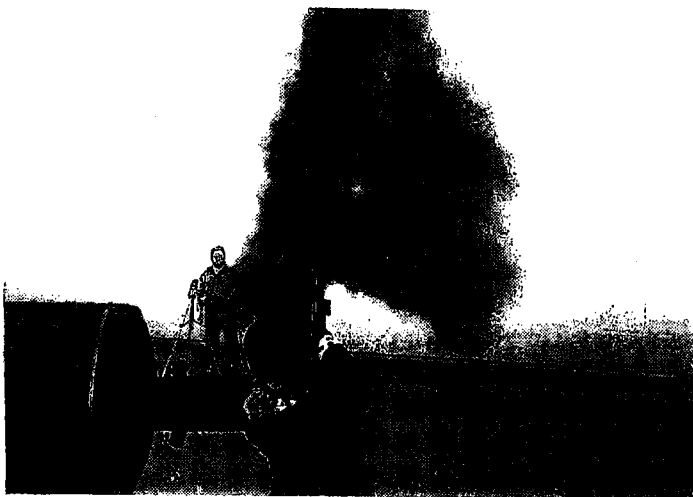


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Fig. _7



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Fig. _9

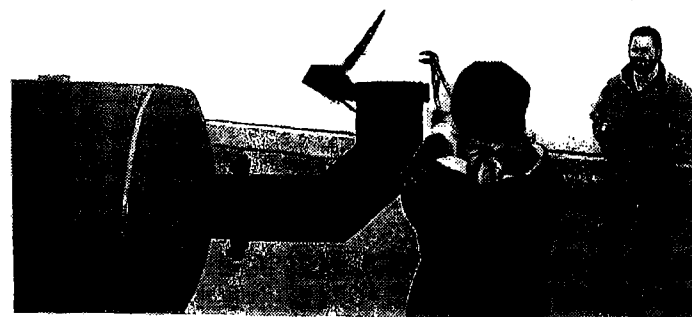


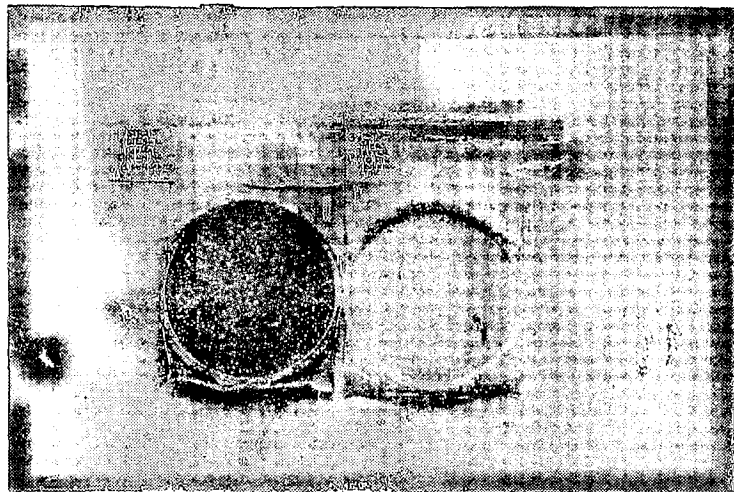
Fig. _8



Fig. _10



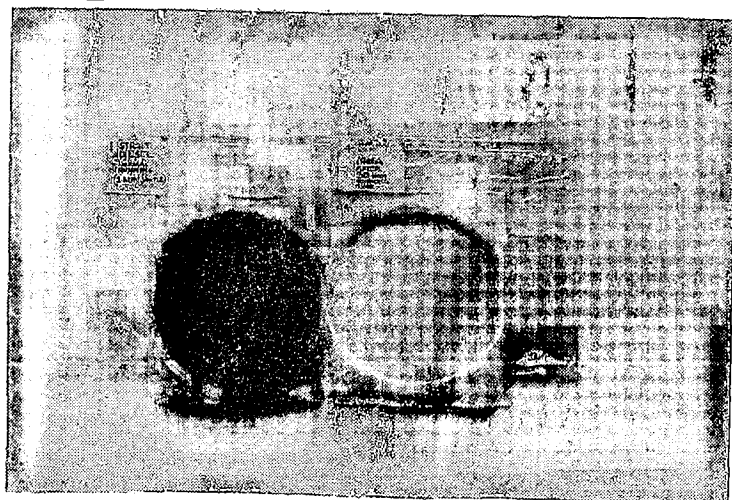
Fig. _11



110A

110B

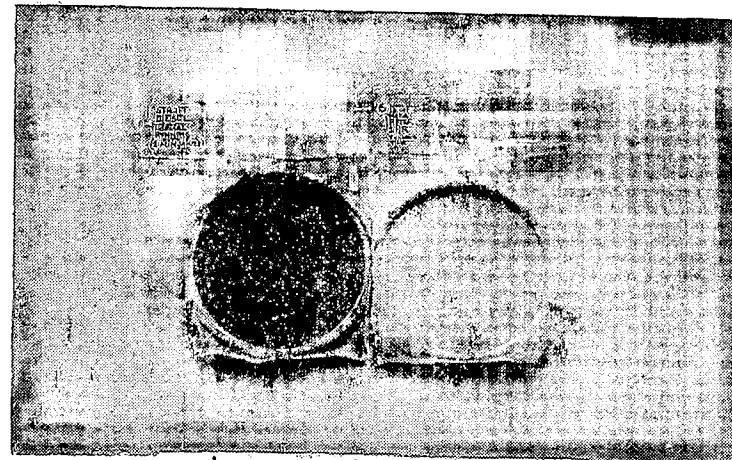
Fig. _12



120A

120B

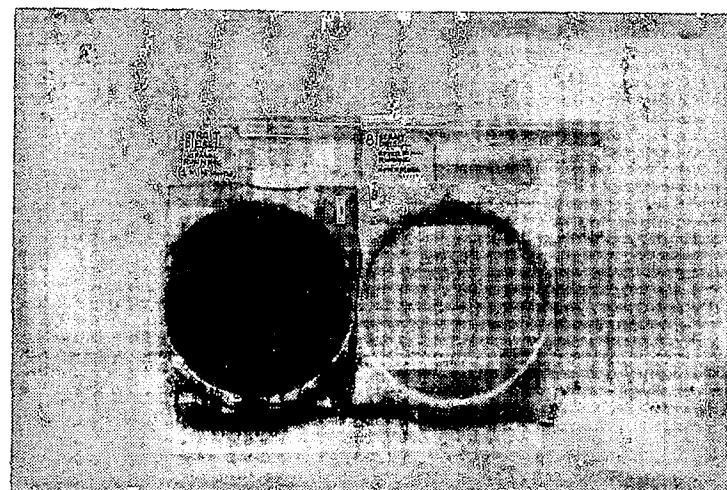
Fig. _13



130A

130B

Fig. _14



140A

140B

Fig. 15

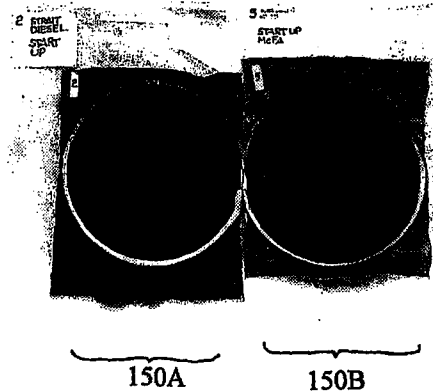


Fig. 16

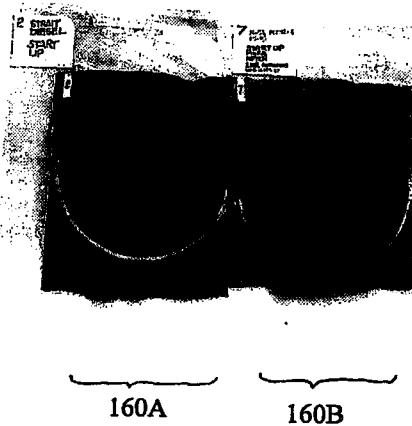


Fig. 17

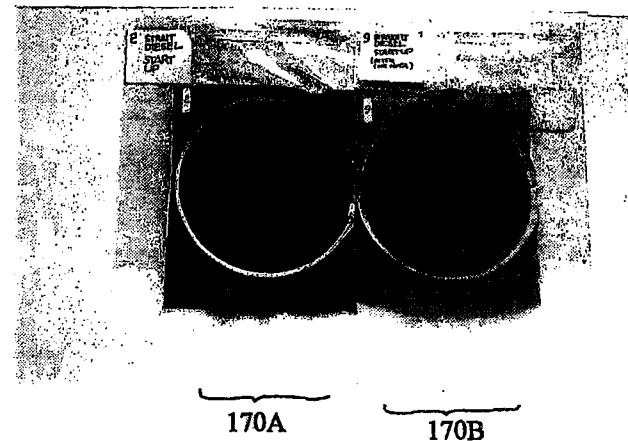
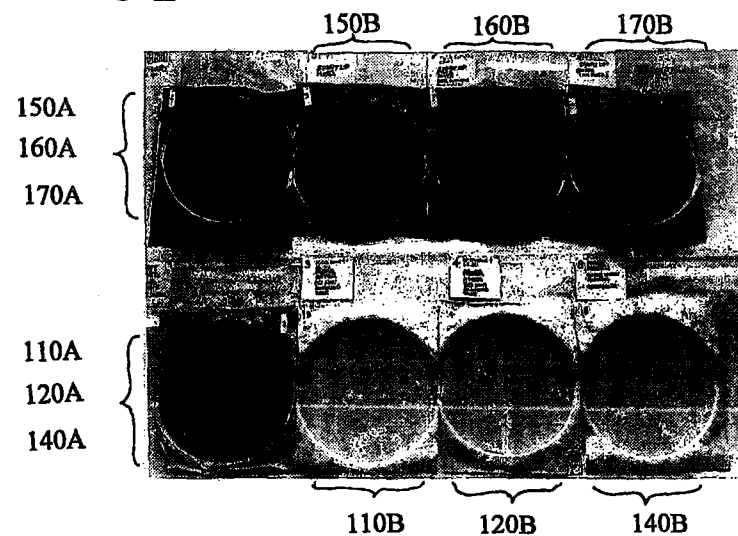


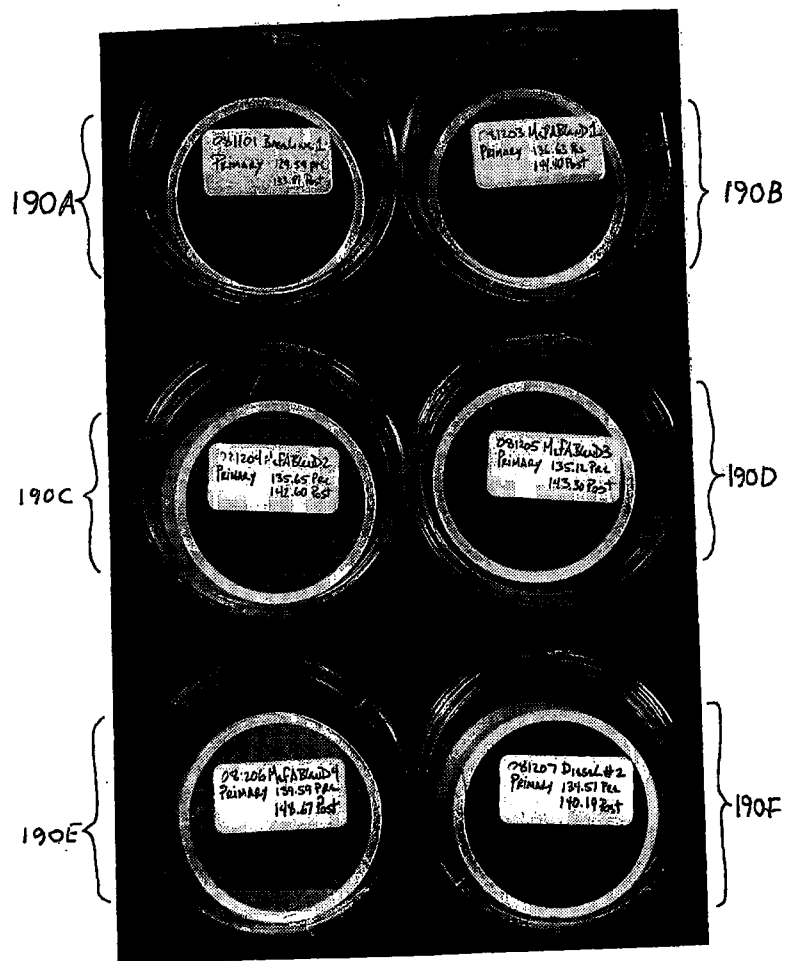
Fig. 18



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Fig. 19



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