

United States Patent

Nixon et al.

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[54] **FUEL EMULSION WITH IMPROVED STABILITY**

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[73] Assignee: Esso Research and Engineering Company

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[52] U.S. Cl. 44/51, 252/308

[51] Int. Cl. C10I 1/32

[58] Field of Search 44/51; 252/308

[56] **References Cited**

UNITED STATES PATENTS

3,416,320 12/1968 Asher 252/308 X

3,458,294 7/1969 Nixon et al. 44/51
3,490,237 1/1970 Lissant 44/51

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[57]

ABSTRACT

Stability of viscous liquid hydrocarbon emulsions, wherein the hydrocarbon is present in a major proportion as the dispersed phase and emulsifiers do not represent more than 2 wt. percent of the total emulsion, is improved by the addition of certain dicarboxylic acid derivatives derived from reaction with amines and alcohols.

11 Claims, No Drawings

FUEL EMULSION WITH IMPROVED STABILITY

FIELD OF THE INVENTION

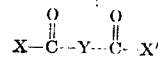
The present invention relates to improving the stability of viscous liquid hydrocarbon emulsions, wherein the hydrocarbon is present in a major proportion as the dispersed phase and emulsifiers do not represent more than 2 wt. percent of the total emulsion. More particularly, this invention is concerned with the addition to liquid hydrocarbon emulsion systems using low emulsifier levels (e.g., 0.5-1.0 wt. percent) of a material useful as an emulsion stabilizer.

The emulsified systems to which the compounds are added are of the type in which a normally liquid hydrocarbon fuel is the dispersed phase and constitutes at least 75 wt. percent of the total emulsion. Said emulsion has as the continuous phase a minor proportion of a polar organic liquid, the latter includ-

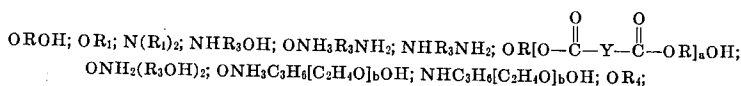
fuels at low emulsifier levels thus permitting the use of lower proportions of high cost emulsifiers.

SUMMARY OF THE INVENTION

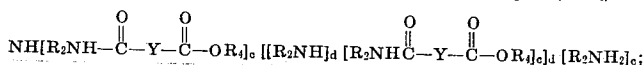
It has now been discovered that the stability of viscous liquid hydrocarbon emulsions, wherein the hydrocarbon is present in a major proportion as the dispersed phase and emulsifiers do not represent more than 2 wt. percent of the total emulsion, is improved by the addition of a material useful as an emulsion stabilizer having the general formula:



wherein X and X' are each selected from the group consisting of



and



ing, but not being limited to, formamide, ethylene glycol, formamide-urea mixtures, glycol-formamide mixtures and the like.

DESCRIPTION OF THE PRIOR ART

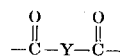
Viscous emulsions of the type wherein the hydrocarbon fuel is the dispersed phase have been found to possess certain advantages particularly in connection with the emulsification of jet fuels for civilian and military aircraft. It has previously been discovered that by emulsifying jet fuels to the extent that the fuel dispersed phase constitutes at least 75 wt. percent of the emulsion while the continuous phase is largely composed of the remainder of the emulsion, a certain safety factor is incorporated into such fuels. Before said discovery, in the crashes of aircraft or in military operations subject to the impact of enemy projectiles on the aircraft, the tendency towards sudden ignition of the atomized and/or vaporized fuel contained in the fuel tanks of such aircraft was great because of the inherent characteristics of the jet fuels. However, it was discovered that when such fuel tanks are filled with stable fuel emulsions which are viscous in nature, the fuel does not readily vaporize or atomize. Thus, the use of fuel emulsions practically reduced to a minimum the tendencies for explosions and burning ordinarily encountered by reason of the military and civilian punctures or ruptures which apply to fuel tanks containing liquid fuels, largely because the fuels in emulsion form have eliminated to substantial degrees the tendency of the stored fuel to vaporize or atomize. Such emulsions are now known in the art and have been prepared using the materials set forth in U.S. Pat. No. 3,429,817, U.S. Pat. No. 3,458,294 and copending application, Ser. No. 813,271, filed Apr. 3, 1969, which are incorporated herein by reference. However, it has been found that at relatively low emulsifier levels (e.g., 0.5-1 wt. percent) the stability of these emulsions is greatly decreased.

The use of about 0.001 to about 1 wt. percent of the amido-ester reaction product of a polyamine and a dialkyl ester of a dicarboxylic acid in fuels as a lubricity additive, and the use of about 0.001 to about 0.4 wt. percent of the reaction product of a dicarboxylic acid and a glycol in fuels, also as a lubricity additive, have been taught in U.S. Pat. No. 3,321,404 and U.S. Pat. No. 3,429,817, respectively. Similarly, U.S. Pat. Nos. 3,281,358; 3,390,083; 3,180,832 and 3,287,273 disclose the preparation of antiwear and lubricity additives from dicarboxylic acids and polyamines; dicarboxylic acids and hydroxy amines; dicarboxylic acids, glycols and alcohols or amines; and dicarboxylic acids and glycols. However, it has heretofore not been known that the use of about 0.25 to about 5 wt. percent of these materials, which are not recognized in the art as emulsifiers, would improve the emulsion stability of emulsified

providing that X and X' are not both OR_1 ; Y is a hydrocarbon radical having one to 42 carbon atoms; R is selected from the group consisting of C_2 - C_{50} straight or branched chain alkylene radicals, C_3 - C_{50} bivalent alicyclic hydrocarbon radicals and $-\text{[R}_2\text{O}]_e$ radicals; R_1 is selected from the group consisting of hydrogen and C_1 to C_6 alkyl radicals; R_2 is a C_2 - C_3 alkylene radical; R_3 is a hydrocarbon radical having two to 20 carbon atoms; R_4 is a hydrocarbon radical having one to 36 carbon atoms; a is a number having a value of one to 25; b has a value of one to 10; c has a value of zero to one; d has a value of zero to five; e has a value of from one to 50; and the sum of all the c's and d's is at least one.

DETAILED DESCRIPTION

In the stabilizing additives of this invention the basic structure is that of a dicarboxylic acid having the general formula



wherein Y is a hydrocarbon radical having one to 42 carbon atoms. Starting with these dicarboxylic acids, the additive compounds for the emulsified fuels are prepared by reacting said acids with various components. For example, they can be prepared by reacting said acids with a glycol such as a C_2 - C_{50} alkane diol and/or C_4 - C_{100} oxa-alkane diol described in U.S. Pat. Nos. 3,180,832; 3,429,817 and 3,287,273. Similarly they can be prepared by reacting said acids with said glycols to form a partial ester and then further reacting the resulting partial ester with ammonia, a C_1 - C_6 alkyl alcohol, a simple primary or secondary C_1 - C_6 alkyl amine or a polyamine to produce a blocked polyester in the manner described in U.S. Pat. No. 3,390,083 for reacting ethylene glycol, a C_{36} dicarboxylic acid and an alcohol. They can also be produced by reacting said acids with C_2 - C_{20} polyamines and/or hydroxy amines as described in U.S. Pat. No. 3,281,358 or by reacting a diester of a dicarboxylic acid with a hydrocarbon polyamine as described in U.S. Pat. No. 3,321,404.

It is preferred for some embodiments of the present invention that the number of carbon atoms between the carboxylic groups of the dicarboxylic acid be in the range of about eight to about 42. Especially preferred are the dimers of a C_{12} - C_{18} unsaturated monocarboxylic acid. Specific examples of these acids are the dimer of linoleic acid, the dimer of oleic acid, the mixed dimer of linoleic and oleic acids and the dimer of dodecadienoic acid. It is also possible to employ dicyclopentadiene dicarboxylic acid. While the foregoing acids are preferred, similar dicarboxylic acids such as "VR-1" described in U.S. Pat. No. 2,833,713 and "D-50" described in

U.S. Pat No. 2,470,849 may be used. The dienic or trienoic monocarboxylic acid, that is polymerized to give the dicarboxylic polymer, can have from 12 to 30 carbon atoms. Extremely suitable dimer acids for use in the present invention are commercially available from Emery Industries, Inc. under the trade name of Empol dimer acids. These dimer acids are available in various grades of dimer acid purity relative to trimer and monobasic acid content. For example, Empol 1014 dimer acid consists of 95 percent dimer acid, a minor proportion of trimer acid and a trace of monobasic acids. Also available are Empol 1018 dimer acid (containing 16 percent trimer and a trace of monobasic acid), Empol 1022 dimer acid (19 to 22 percent trimer and 2 to 5 percent monobasic acids) and Empol 1025 dimer acid (containing the same trimer acid content as Empol 1022 but containing only a trace amount of monobasic acid). The specifications and typical compositions of the Empol dimer acids discussed above are given in table I.

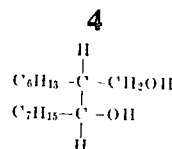
TABLE I

	Empol 1014	Empol 1018	Empol 1022	Empol 1024
Neutralization Equivalent	288-294	287-299	289-301	289-301
Acid Value	191-195	188-196	186-194	186-194
Saponification Value	195-199	192-198	191-199	191-199
Color, Gardner 1953 max.	8	8	9	9
Monobasic Acids (Max. Percent)	1.5%	1%	2-5%	1%
Dimer Acid	95	83	77	79
Trimer Acid	4	17	20	21
Monobasic Acids	1	Trace	3	Trace
Dimer:Trimer Molar Ratio	36:1	7:1	6:1	6:1

The commercial dimer acids discussed above are generally produced by polymerization of unsaturated C₁₈ fatty acids to form C₃₆ dibasic dimer acids. Depending on the raw materials used in the commercial process, the C₁₈ monomeric acid may be linoleic acid or oleic acid or mixtures thereof. The resulting dimer acids can therefore be the dimer of linoleic acid, the dimer of oleic acid or a mixed dimer of linoleic and oleic acid. Furthermore as can be seen from the above, table I, these commercially available "dimer acids" are not necessarily 100 percent pure dimer acids and dimer acids containing minor proportions of trimer acid and monobasic acids can be utilized in the practice of the present invention. However, it is essential that the amount of dimer acid present in the acid composition be at least 50 percent and preferably above 75 percent, such as 95 percent by weight. It is to be understood that, under certain circumstances, these dicarboxylic acids can be substituted acids such as with bromine, fluorine or a hydroxy group.

Specific examples of the foregoing dicarboxylic acids are: dimer acids (e.g., dilinoleic acid and dioleic acid); straight chain aliphatic dibasic acids, such as malonic acid; succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid and dodecadienoic acid; benzene polycarboxylic acids, such as phthalic acid, isophthalic acid, terephthalic acid, hemimellitic acid, trimellitic acid, trimelic acid, prehnitic acid, mellophanic acid, pyromellitic acid, benzene pentacarboxylic acid and mellitic acid; and other such as diphenic acid, diglycolic acid and d-tartaric acid.

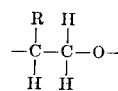
As indicated, one embodiment of this invention employs an emulsion stabilizer formed by reacting a dicarboxylic acid with a C₂-C₅₀ alkane diol and/or C₃-C₁₀₀ oxa-alkane diol. Thus, each mole of the acid is reacted with one or two HOROH groups wherein R is selected from the group consisting of C₂-C₅₀ straight or branched chain alkylene radicals, C₃-C₅₀ bivalent alicyclic hydrocarbon radicals and [R₂O]_e radicals, R₂ is a C₂-C₃ alkylene radical, and e has a value of from one to 50. A satisfactory glycol has 16 carbon atoms and the general formula:



wherein the C₆ and C₇ alkyl groups are branched. Other suitable diols are oxa-alkane diols obtained, for example, by hydrolysis of ethylene oxide, propylene oxide or other epoxy compounds. These diols may have molecular weights between 200 and 2,000. An example is 3,6,9-trioxa-1,4,7,10-tetramethyl undecane-1,11-diol.

The glycols used are preferably oil insoluble. Thus, the glycol reacted with the dicarboxylic acid may be an alkane diol or an oxa-alkane diol, straight chain or branched. These alkane diols will generally have from about two to eight carbon atoms, preferably two to five carbon atoms in the molecule.

The oxa-alkane diol can have four to 100, preferably four to 40, carbon atoms with periodically repeating groups of:

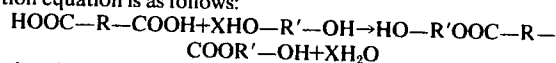


wherein R is H or CH₃.

The preferred alkane diol is ethylene glycol and the preferred oxa-alkane diol is 4-oxa-heptane diol-2,6. Other specific satisfactory glycols are, for example, propylene glycol, polypropylene glycol, polyethylene glycol and the like.

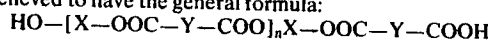
The molar quantities of the dicarboxylic acid and glycol reactants may be adjusted so as to secure either a complete diester or a partial ester.

The additives of the present invention comprising a reaction product between a dimerized dicarboxylic acid and a glycol may be produced by various techniques. Turning now to the embodiment wherein a diester of a dimeric dicarboxylic acid is used, as previously indicated, the molar quantities of reactants are adjusted in this embodiment so as to secure a complete diester. For example, one process is to reflux an excess of the diol with the selected dioic acid at 80° C. in the presence of benzene as diluent and toluene sulfonic acid as catalyst until the theoretical amount of water has been produced in a water trap in the reflux condenser. The diluent is then stripped off under vacuum at 40° C. The general reaction equation is as follows:



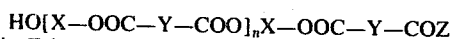
wherein R is the radical of a glycol and R' is the hydrocarbon part of the dimer acid and X is at least two. While either the dicarboxylic acid or the ester product may be hydrogenated, it is preferred that the dicarboxylic acid be hydrogenated prior to esterification when producing the diester. This hydrogenation may be accomplished by any suitable process known to the art. For example, the acid may be reduced with hydrogen gas over platinum catalyst at a temperature in the range from 20° to 100° C. in a steel bomb. The hydrogen pressure in the system may range from about 10 to 300 pounds. Another method by which hydrogenation may be accomplished is by the use of lithium hydride using conventional techniques at ambient temperatures.

Another preferred embodiment of this invention employs an emulsion stabilizer prepared by reacting said acids with said glycol to form a partial ester and then further reacting the resulting partial ester with an alcohol or amine. Generally speaking, the simple esterification of the dicarboxylic or dimer acid with the glycol is carried out using equimolar amounts of the two reactants, with the esterification being continuous, usually under refluxing conditions until more than 1 but less than 2 moles of water of reaction have been produced per mole of acid and per mole of glycol employed. By so controlling the reaction conditions, catalyst concentration, and the like, the polyesterification reaction results in a partial ester being formed. The polymeric, partially esterified composition is believed to have the general formula:



wherein X is the alkylene portion of from two to 50 carbon atoms of the glycol employed originally and Y is the alkylene portion of the acid and wherein n is an integer ranging from about 1 to about 25. Preferably, n is between about 1 and about nine. The desired upper limit of n depends on the solubility limitation in the particular hydrocarbon oil in which the additive is to be incorporated.

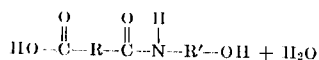
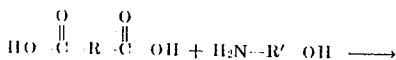
The above-identified polymeric partial ester is then further reacted with ammonia, with a primary or secondary amine under amidation conditions, or with a monohydric alcohol such as methanol or ethanol in order to block the free carboxyl groups with an amino group by reacting the OH group of the free carboxyl radicals or by esterification with the alcohol. In other words, the carboxyl hydrogens in the above polymerized partial ester are replaced by an alkyl group of one to six carbon atoms which would be formed if a monohydric alcohol were employed or the OH of the carboxyl groups would be replaced by a $\text{NR}'\text{R}''$ wherein R' would be a $\text{C}_1\text{--C}_6$ alkyl group or hydrogen, and R'' would be a $\text{C}_1\text{--C}_6$ alkyl group or hydrogen, or the R' 's could be the residue of hexamethylene tetramine or the like. The blocked ester would have the formula:



wherein Z is an $-\text{O}$ alkyl, $-\text{NH}_2$, $-\text{NH}(\text{alkyl})$ or $-\text{N}(\text{alkyl})_2$.

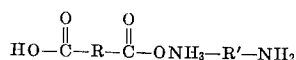
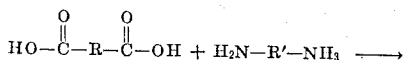
In the embodiment of the invention in which said emulsion stabilizers are the reaction product of said acids with $\text{C}_2\text{--C}_{20}$ polyamines and/or hydroxy amines, the amine compounds for use in conjunction with the diacids of the present invention are selected from the class consisting of polyamines and hydroxy amines such as amino alcohols, diamines, polyglycol amines, and dialkanol amines.

The dicarboxylic acid amino alcohol reaction product may be prepared by reacting 1 mole of dimer acid with 1 mole of an amino alcohol as follows:



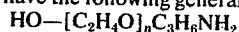
The preferred amino alcohols are those alcohols having from about two to 20 carbon atoms and R' may be derived from aliphatic, alicyclic or aromatic hydrocarbons. Specific amino alcohols which are desirable are monoethanolamine, N-aminoethyl ethanolamine, p-amino phenol, 4-amino-1-butanol, 5-amino-1-pentanol, 10-amino-1-decanol, and amino isopropanol.

The diacid diamine reaction products in accordance with the present invention may be made by reacting 1 mole of a dicarboxylic acid with 1 mole of a diamine as follows:



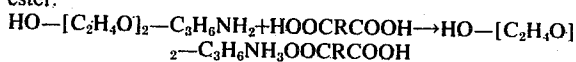
R may be a bivalent aliphatic, alicyclic or aromatic hydrocarbon radical containing from nine to 42 carbon atoms. R' may be a bivalent aliphatic, alicyclic or aromatic hydrocarbon radical containing from two to 20 carbon atoms. Examples of suitable diamines are thylene diamine, propylene diamine, 1,4 butane diamine and 1,6 hexane diamine. In general, the preferred structure for both the diacids and diamines is $\alpha\text{--}\omega$.

The polyglycolamines for use in conjunction with the present invention have the following general structure:

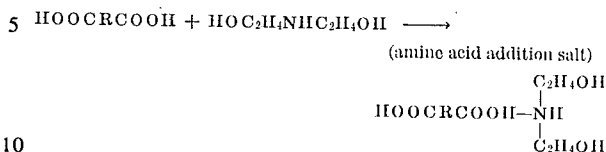


wherein n has a value of one to 10.

An example of a commercially available product of this type is polyglycolamine H-163 ($n=2$) made by the Union Carbide Chemicals Company. This may be reacted with a dibasic acid to form an amine acid addition salt or possibly even a partial ester.



The dicarboxylic acid dialkanol amine reaction product for use in conjunction with the present invention has the following general formula:



Here again the number of carbon atoms in the dialkanol amine may vary in the range from about two to 20.

In another preferred embodiment of this invention, the emulsion stabilizer is the amido-ester reaction product of a hydrocarbon polyamine and a diester of said acids.

Examples of alcohols which may be used to esterify the dicarboxylic acids to form said diester intermediates are methanol, ethanol, propanol, isopropanol, butanol, isobutanol and pentanol. Other alcohols are benzyl alcohol, cyclohexanol and 2-ethyl hexanol. These esters may also be mixed esters such as monoethyl monopropyl ester of the dimer of a dicarboxylic acid such as the dimer of linoleic acid. Said alcohols will generally contain about one to about 36 carbon atoms and preferably contain about one to about eight carbon atoms. Very desirable intermediate esters produced from said alcohols include the dimethyl ester of dilinoleic acid, the dimethyl ester of dioleic acid and the dimethyl ester of the mixed dimer of linoleic and oleic acids. The polyamine is a compound containing two or more amine groups. Some broad examples of polyamines are diamines, triamines, tetramines, and pentamines. Specific examples are dimer diamines made from dilinoleic acid or dioleic acid, tetraethylene pentamine, propylene diamine, imino-bis-propyl amine, hexamethylene tetramine, 1,4-bis (aminomethyl)-cyclohexane, 1,8-p-menthane diamine and fatty acid 1,3 propylene diamine compounds. It is also possible to use hydroxy amine compounds since these are also difunctional.

The polyamines may contain aliphatic, alicyclic or aromatic groups or mixed groups such as alkyl-aromatic. The polyamines and polybasic acid esters may contain alkyl, aryl and alicyclic groups or mixed alkyl-aryl, etc., groups. Examples of the general types of polyamine compounds which may be used are shown below:

- 50 $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ where n has a value of about two to about 20;
- $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{N})_n\text{CH}_2\text{CH}_2\text{NH}_2$ where n has a value of zero to about five;
- 55 Tallow 1,3 propylene diamines (e.g., Duomeens);
- Polyamino benzenes;
- Phenylene diamines; and
- Dimer diamine.

Thus, in essence, this embodiment of the present invention uses a reaction product between a dialkyl ester of a dicarboxylic acid and a polyamine, preferably an oil-insoluble polyamine. A very desirable reaction product is that obtained between di-2-ethyl-hexylsebacate and tetraethylene pentamine.

Nonlimiting examples of additives used in other embodiments of this invention include the mono-beta-hydroxy ethyl ester of C_{36} linoleic dimer acid, the bis (beta-hydroxy) ethyl ester of C_{36} oleic dimer acid, the reaction product of equal molar amounts of C_{36} linoleic dimer acid and diethanol amine, etc.

As hereinbefore stated, the additives of this invention, which improve stability and lubricity, are intended for use in viscous liquid hydrocarbon emulsions containing a high percentage of an internally dispersed hydrocarbon phase within a continuous phase and not more than 2 percent emulsifiers. An emulsion containing a high percentage of an internal dispersed phase exerts a phenomenon known as "yield stress" (see ASTM D2507 "Tentative Definition of Terms Relating to Rheological Properties of Gelled Rocket Propellants.") which might be looked upon as being that force necessary to overcome the viscosity inertia of the stable emulsion. It is measured in dynes per square centimeter and aids in defining the

"viscosity" of the stable emulsion. Under conditions of low shearing stress, such an emulsion will not flow freely. When a sufficiently large shearing stress is applied, the "apparent viscosity" of the emulsion decreases and the material will flow much more readily. If a critical rate of shear is not exceeded, so as to break down the emulsion, the material will regain its much more viscous state once the shear stress is removed.

It is to be noted that the highly viscous, or pseudoplastic, emulsions which the additives of this invention stabilize are to be distinguished from gels. A gel consists of a solid three-dimensional network intertwined with a similar liquid network wherein neither network is entirely within the other. When a gel is made to flow under stress, the interconnectivity of the networks is broken down and must be reestablished in order for the gel to set again. In contrast, in a pseudoplastic emulsion of the type involving the present invention, each droplet of the dispersed phase is actually inside the continuous phase at all times, and flow under stress merely involves a temporary change of geometric configuration.

Yield stress values are determined by the need to have a viscosity that is practical for pumping through a conventional fuel system of fuel pumps and fuel lines and yet provide a fuel emulsion that will not flow readily through penetrations of the wall of the fuel tank. For conventional jet aircraft, both civilian and military, yield stress values in the range of about 800 to 4,000 are particularly useful. The most desired yield stress is one that will restrict the flow out of a punctured, ruptured or split fuel tank or fuel line to a moderate rate under the existing hydrostatic head so that the fuel will not spray and form the ball of highly inflammable mist that usually occurs with an unmodified fuel. The nature of the flow with the emulsion of the invention is much akin to the flow of toothpaste from the conventional collapsible tube, forming a mass or pile instead of a rapidly spreading puddle. Thus, while the emulsion mass is still capable of catching on fire, it will be contained within an area that can be much more readily brought under control than in the case of unthickened fuel.

The dispersed phase of the emulsion can be any liquid which is substantially immiscible with the liquid employed as the continuous phase.

The preferred hydrocarbons that form the dispersed phase in the emulsions of the present invention include those boiling within the range of about 70° to 750° F., e.g., petroleum fractions, such as gas oils, kerosene, motor gasoline, aviation gasoline, aviation turbojet fuels, diesel fuels, Stoddard solvent, and the like, as well as coal tar hydrocarbons such as coal tar solvent naphtha, benzene, xylene, hydrocarbon fuels from coal gasification, shale oil distillates, and the like. Gasoline is defined as a mixture of liquid hydrocarbons having an initial boiling point in the range of about 70° to 135° F. and a final boiling point in the range of about 250° to 450° F. Most usually gasolines are identified as either motor gasolines or aviation gasolines. Motor gasolines normally have boiling ranges between about 70° and 450° F., while aviation gasolines have narrower boiling ranges between about 100° and 330° F. Gasolines are composed of a mixture of various types of hydrocarbons, including aromatics, olefins, paraffins, isoparaffins, and naphthenes. Stoddard solvent generally has a boiling range of about 300° to 400° F. Diesel fuels include those defined by ASTM Specification D-975. Jet fuels generally have boiling ranges within the limits of about 150° to 600° F. Jet fuels are usually designated by the terms JP-4, JP-5, or JP-6. JP-4 and JP-5 fuels are defined by U.S. Military Specification MIL-T5624-G. Aviation turbine fuels boiling in the range of 200° to 550° F. are defined by ASTM Specification D-1655-59T.

While it is contemplated that the invention is best applicable to the preparation of hydrocarbon fuels as the dispersed phase, it is not limited thereto. Such emulsions have been found to be stable at temperatures ranging from -65° to +140° F. for periods in excess of 90 days. The dispersed phase may be a halogenated hydrocarbon such as the perchlorinated or perfluorinated lower alkanes and alkenes. Tetrafluoroethane,

tetrachloroethylene, hexachloroethane, the perfluoro butanes and pentanes and the like are examples of liquids that may be emulsified in water or formamide as the continuous phase. Such emulsions find utility as drycleaning compositions. Additionally, oxygen-containing derivatives of hydrocarbons such as methyl isobutyl ketone, lauryl alcohol, stearyl alcohol, oleic acid, myristic acid and stearic acid may be the dispersed phase with water or formamide being the continuous phase. If necessary, sufficient heat may be applied during emulsification to insure a liquid phase condition for all the components.

Nonaqueous, highly polar organic liquids constitute the continuous phase of the emulsion. All of these liquids are, of course, immiscible with respect to the hydrocarbon fuel or hydrocarbon derivative constituting the dispersed phase. These materials are characterized by having dielectric constants greater than 25 and solubility parameters greater than 10. Most of them will have freezing points of 40° F. or lower so that the emulsions will be stable at relatively low temperatures. Representative examples of the compounds which may be employed as the continuous phase are: formamide, dimethyl formamide, dimethyl sulfoxide, dimethyl acetamide, propylene carbonate, formic acid, glycerol, glycidol, ethylene glycol, propylene glycol, 2-pyrrolidone, or mixtures of two or more of such materials. The continuous phase materials can be still further modified and, in many instances, are advantageously modified by adding thereto between about 0.5 and 40.0 percent, based upon the weight of the aforementioned continuous phase material, of a material such as urea, oxamide, and guanidine, or other solid amide, provided that the nature of the amide employed and the amount of the amide used are such that when it is added to the aforementioned continuous phase materials or mixtures of materials, the mixture still remains liquid under the emulsification conditions prevailing. A suitable continuous phase constitutes 80 percent formamide and 20 percent urea. The properties of the polar organic material, which expression is intended to include water as compared, for example, with JP-4 jet fuel, are as follows:

Substance	Freezing point, ° F.	Boiling point, ° F.	Dielectric constant	Solubility parameter ¹
Formamide.....	32	451	109	18
Dimethyl formamide.....	-70	392	37	12
Dimethyl sulfoxide.....	65	385	45	13
Formic acid.....	47	213	58	12.1
Glycerol.....	32	564	45	16.5
Ethylene glycol.....	1	387	41	14.2
JP-4 jet fuel.....	<-70	140 (IBP)	2	7
Water.....	32	212	80	23.4

¹ Calculated as square root of energy of vaporization per molar volume e.g. cal/cc. by method of J. H. Hildebrand "Solubility of Non-Electrolytes", 3rd Edition, Reinhold Publishing Corporation, New York, 1950.

² Crystallizes slowly at this temperature, melting point of crystals is higher.

The emulsification of a hydrocarbon fuel as a dispersed phase in a continuous phase material, as defined above, is not satisfactorily accomplished without the presence of one or more organic emulsifiers, dispersants or surfactants. The materials successfully used should be essentially nonash forming in nature and if traces of them are contained in the fuel after demulsification, they should not form residues in the engines wherein the fuel is combusted. Hence, the use of non-metallic emulsifiers is desirable. The best balance of force of attraction between the hydrocarbon phase and the continuous phase of the emulsion is obtained by using a combination of two or more emulsifiers. For most satisfactory results, the lipophilic portion of the emulsifier must closely match the particular hydrocarbon or hydrocarbon fraction being dispersed. To attain the proper balance between lipophilic and nonlipophilic (i.e., hydrophilic) forces in the emulsifier system, it is convenient to use the scale of HLB values known to the emulsifier

TABLE II

	Composition			Yield stress, dynes/cm. ² at room temperature		Vibrator stability percent separation at 360 cycles/ min. and 2g amplitude		Thermal stability, percent separation	
	JP-4	Percent emulsifier	Percent stability additive	Ini- tial	After 2 days	30 min- utes	1 hour	2 days at 140° F.	2 days at -65° F.
Example:									
1.....	97.0	0.5 emulsifier A	0.5 amine-ester adduct ²	3,800	1,400	0.0	0.0	0.0	0.0
2.....	97.0	0.5 emulsifier B	do	3,120	1,110	0.0	0.0	0.0	0.0
Comparative emul- sion A.	97.0	1.0 emulsifier A	0	3,550	970	1.0	1.0	50	50
Example:									
3.....	87.5	0.5 emulsifier A	10.0 polyester adduct ⁴	1,550	1,500	0.0	0.0		
4.....	29.0	1.0 emulsifier A	5.0 polyester adduct	2,700	2,400	0.0	0.0		
5.....	95.5	0.5 emulsifier A	2.0 polyester adduct	1,500	1,475	0.0	0.0		
Comparative emul- sion B.	97.5	do	0	1,600	1,025	100	100		

¹ Emulsifier A—Blend of 50 weight percent of Atlas IL-851 emulsifier (which is a mixture of ethoxylated sorbitan monooleate and sorbitan monooleate) and 50 weight percent of ethoxylated (12 moles) tridecyl alcohol (1 mole).

² Amine-ester adduct—Reaction product of 37.8 g. tetraethylene pentamine and 79.6 g. Di-2-ethyl-hexyl sebacate (heated together for 48 hrs. under reflux at atmospheric pressure and 150° C. in a 250 ml. round bottom flask with stirring).

³ Emulsifier B—28/72 blend of Atlas Span 80 & Tween 80.

⁴ Polyester Adduct—Commercially bought adduct described as 50% polyester of dilinoleic acid ("Empol 1022" C36 dimer acid) and ethylene-glycol in which the residual carboxyl groups, remaining after polyesterification, are blocked by methylation, dissolved in 50% naphthenic base oil having a viscosity at 210° of 90 SUS available as OA-201 from Robinson Bros. of the United Kingdom.

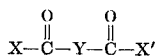
Table II serves to demonstrate that while fuel emulsions tend to be unstable at low emulsifier levels, this instability is eliminated by the emulsion stabilizers of this invention. As can be seen from comparative emulsions A and B, stability increases with increased emulsifier concentration. However, emulsifiers are expensive and even 1 percent of emulsifier A does not stabilize the emulsion. On the other hand, 0.5 percent of emulsifier A and 0.5 percent of a less expensive amine ester adduct produces a completely stable emulsion. This unexpected stabilizing effect is achieved despite the fact that said stabilizers are not recognized in the art as emulsifiers and in fact are not effective by themselves as emulsifiers for the present system.

Example 2 serves to illustrate the use of these additives in other emulsifier systems and examples 3, 4 and 5 illustrate their use in conjunction with different concentrations of dispersed fuel.

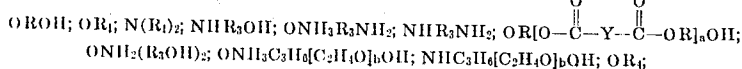
While particular embodiments of this invention are shown in the examples, it will be understood that the invention is obviously subject to the variations and modifications disclosed above without departing from its broader aspects and, therefore, it is not intended that the invention be limited to the specific modifications which have been given above for the sake of illustration, but only by the appended claims.

What is claimed is:

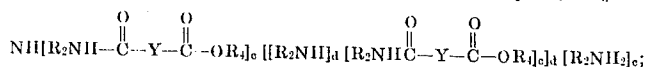
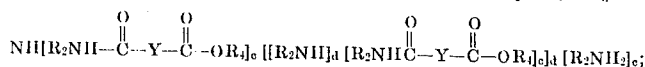
1. In a hydrocarbon emulsion which comprises about 75 to 99 wt. percent of a liquid hydrocarbon boiling within the range of 70° to 750° F. as a dispersed phase, about 0.5 to 20 wt. percent of a polar organic liquid as the continuous phase, said organic liquid being immiscible with said hydrocarbon and having a dielectric constant greater than 25 and a solubility parameter in excess of 10, and from about 0.25 to about 2 wt. percent of organic emulsifier, the improvement comprising having in admixture therewith about 0.25 to about 5 wt. percent of a material useful as an emulsion stabilizer having the general formula:



wherein X and X' are each selected from the group consisting of



and



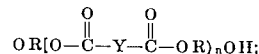
providing that X and X' are not both OR₁; Y is a hydrocarbon radical having one to 42 carbon atoms; R is selected from the group consisting of C₂-C₅₀ straight or branched chain alkylene radicals, C₅-C₅₀ bivalent alicyclic hydrocarbon radicals

and $-\text{[R}_2\text{O]}_e$ radicals; R₁ is selected from the group consisting of hydrogen and C₁ to C₁₀ alkyl radicals; R₂ is a C₂-C₄ alkylene radical; R₃ is a hydrocarbon radical having two to 20 carbon atoms; R₄ is a hydrocarbon radical having one to 36 carbon atoms; a is a cardinal number having a value of one to 25; b has a value of one to 10; c has a value of zero to one; d has a value of zero to five; e has a value of from one to 50; and the sum of all the c's and d's is at least one.

2. The composition of claim 1 wherein both X and X' are OROH.

3. The composition of claim 3 wherein R is the hydrocarbon skeleton of a C₂-C₈ glycol.

4. The composition of claim 1 wherein X is

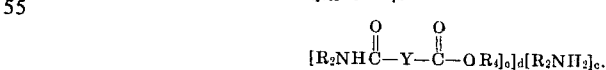
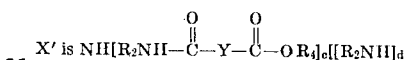


X' is selected from the group consisting of OR₁ and N(R₁)₂; and R is the hydrocarbon skeleton of a C₂-C₈ glycol.

5. The composition of claim 4 wherein Y is a C₂₂ to C₃₄ group of a C₁₂ to C₁₈ dimer acid, R is the hydrocarbon skeleton of a C₂-C₅ glycol and R₁ is a C₁-C₆ alkyl group.

6. The composition of claim 5 wherein Y is a C₃₄ group of a C₁₈ dimer acid; n has a value of about five to about 20; R is the hydrocarbon skeleton of a C₂ glycol; and R₁ is a C₁ alkyl group.

7. The composition of claim 1 wherein X is OR₄; and



8. The composition of claim 7 wherein R₄ is a hydrocarbon radical having one to eight carbon atoms and R₂ is a C₂ alkyl group.

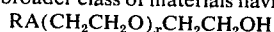
9. The composition of claim 8 wherein said emulsion stabilizer is the amido-ester reaction product formed by reacting di-2-ethylhexyl sebacate and tetraethylene pentamine.

10. The composition of claim 9 wherein said liquid hydrocarbon is a jet fuel.

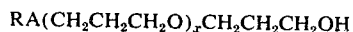
11. The composition of claim 1 wherein X is OR₁ and X' is selected from the group consisting of NHR₃OH, ONH₃R₃NH₂, NHR₃NH₂, ONH₂(R₃OH)₂, ONH₃C₃H₆[C₂H₄O]_bOH and NHC₃H₆bqC₂H₄O]_bOH.

art. These are discussed by W. C. Griffin in the Journal of the Society of Cosmetic Chemistry, Dec., 1948, page 419; also in Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 8, pages 131-133 (1965). Desired HLB values can be obtained by using two or more emulsifiers in combination. Emulsifiers and emulsifier combination which give HLB values in the range of 11-16 are satisfactory for producing a stable emulsion in the present invention when the continuous phase material is formamide. Formamide gives the greatest latitude in the selection of emulsifiers that may be used. This is believed to be because of the optimum combination of strong hydrogen bonding and polarity in formamide. Mixtures of formamide and solid amides such as urea appear to give the most satisfactory emulsions when using nonionic emulsifiers having HLB values in the 11-14 range. With polar organic liquids within the scope of this invention that are used in conjunction with amides or with small amounts of water, such as ethylene glycol, the effective HLB value will depend on the particular liquid selected and will vary with the proportion of water or amide to the said organic liquid constituting the continuous phase.

Among the surfactants or emulsifiers that may be employed in the present invention are included alkylphenyl, polyethylene glycol ethers such as Tergitol NPX of Carbide and Carbon Company, polyethylene polyoxypropylene glycol such as Pluronic L-64 of Wyandotte Chemical Company, resin acid esters of polyoxyethylene glycol such as Thofat 242/25 of Armour Industrial Chemical Company, and alkylphenyl polyethoxy alkanols such as Triton X-102, which is iso-octyl phenyl polyethoxy ethanol, i.e., the reaction product of iso-octylphenol and ethylene oxide. The alkyl phenyl polyalkoxy alkanols are obtained by reacting 5 to 15 molar proportions of a C₂ to C₃ alkylene oxide with 1 molar proportion of an alkyl phenol having a C₈ to C₁₂ alkyl group, e.g., the reaction product of 6 moles of propylene oxide with 1 mole of dodecyl phenol, the reaction product of a mixture of 5 moles of ethylene oxide and 5 moles of propylene oxide with 1 mole of nonyl phenol, and the reaction product of 8 to 10 moles of ethylene oxide with 1 mole of iso-octyl phenol. These are included within a broader class of materials having the formulas:



or



where R is a C₈ to C₁₈ hydrocarbon group, A is oxygen or sulfur and x is eight to 20.

Other emulsifiers include the fatty acid esters of sorbitan, such as sorbitan monolaurate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monooleate, and the alkoxylated fatty acid esters of sorbitan such as polyoxyethylene sorbitan monostearate, tristearate or trioleate. The various sorbitan esters of fatty acids are well known to the art as Spans, and the polyoxyethylene derivatives of the sorbitan esters of fatty acids are well known as Tweens. Still other suitable emulsifiers include N-alkyl trimethylene diamine dioleate of Armour and Company, octakis (2-hydroxy propyl) sucrose, the condensation products of fatty acid amides and ethylene oxide, the ethoxylated fatty alcohols, polyoxyethylene monostearate, polyoxyethylene monolaurate, propylene glycol mono-oleate, glycerol monostearate, ethanolamine fatty acid salts, stearyl dimethyl benzene ammonium chloride, various gums such as gum tragacanth, gum acacia, etc. Where the presence of metal is not objectionable in the emulsion, metal-containing emulsifiers can also be used, such as sodium dioctyl sulfosuccinate (Aerosol OT) or disodium N-octadecyl sulfosuccinamate (Aerosol 18).

An extensive list of emulsifiers together with their HLB values is given in Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 8, pages 128-130 (1965). From this list it is possible to select those that either alone or in admixture will give an HLB value suitable for use in the present invention.

The liquid hydrocarbon emulsions of the present invention using formamide, formamide-solid amide mixtures, forma-

amide-glycol mixtures and the like, as the continuous phase will generally contain the following broad and preferred ranges of components:

Component	Wt. % Concentration	
	Broad	Preferred
Dispersed Phase	75-99	85-98.5
Continuous Phase	0.5-20	0.5-8
Emulsifier	0.25-2	0.5-1
Stabilizing Additive	0.25-5	0.5-1

The above ranges are not necessarily attainable without regard to the specific types of substances selected for use as the initial components of the emulsion. Thus, where JP-4 jet fuel is the dispersed phase component and a mixture of formamide containing 20 percent urea constitutes the continuous phase component, the ranges may be over the entire range above stated; whereas, if JP-4 fuel is the dispersed phase and formamide containing 35-50 percent urea is the continuous phase, the selection of the relative amounts of dispersed phase would require that in producing a stable emulsion, said emulsion would contain a final concentration of the dispersed phase toward the lower end of the above-stated ranges while the continuous phase would be correspondingly toward the higher end of the amounts specified in the above ranges.

The components of the emulsion can be added in any order desired or all of them can be added simultaneously as an admixture. Thus, it is possible to combine the stability additive of this invention with the hydrocarbon phase and the emulsifiers with the continuous phase material or to add the stability additive along with the emulsifier to the continuous phase, and then to add the hydrocarbon fuel mixture to the continuous phase. Alternatively, with two emulsifiers, one of which is lipophilic and the other hydrophilic, the lipophilic emulsifier can be added to the hydrocarbon phase and the hydrophilic emulsifier added to the continuous phase and then the two phases can be combined. It is preferred that only a portion of the hydrocarbon fuel ultimately to become the dispersed phase be added in the initial emulsification operation, although all of the continuous phase ultimately to be incorporated into the final emulsion can be added in the first stage of emulsification. For example, in producing a gallon (2,500 cc.) of emulsion, the hydrocarbon fuel can be added to about 60 cc. of the continuous phase at a rate of about 10 cc. per minute and after the first minute or two the input of hydrocarbon fuel can be increased by increments of 10 cc. per minute until a rate of 40 cc. per minute is reached. The additional rate can then be held at 40 cc. per minute for about 50 minutes until the emulsion is completed. Similarly, the methods described in U.S. Pat. No. 3,416,320 or U.S. Pat. No. 3,458,294 could be used.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The nature of the invention will be further understood when reference is made to the following examples which include preferred embodiments which are not to be construed as a limitation of the invention.

Examples

In all of the following comparative emulsions (all percentages are weight percent), the base emulsion was composed of JP-4 jet fuel, as the dispersed phase, 0.4 percent of urea and 1.6 percent of formamide as the continuous phase, and various percentages of emulsifiers and stabilizing additives as indicated. All emulsions were prepared and their characteristics measured at room temperature, unless otherwise noted. In preparing these emulsions the amine-ester adduct was added to the continuous phase along with the emulsifiers while the polyester adduct was added to the hydrocarbon phase.