

1

3,490,237

THIXOTROPIC OIL-IN-WATER EMULSION FUELS
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U.S. Cl. 60—217

10 Claims

ABSTRACT OF THE DISCLOSURE

An improved thixotropic hydrocarbon-in-water emulsion fuel, the hydrocarbon being present in an amount of at least 80% by volume of the emulsion, comprising, in addition to the hydrocarbon, water, emulsifying agent and an additive, or a plurality of additives, such as corrosion inhibitors, anti-freeze, biocides, anti-knock compositions, anti-icing compositions, anti-oxidants, lubricating additives, and multipurpose additives having at least two of the properties of said additives and compositions, and mixtures of at least two of said additives and compositions; and also the method of providing power by burning said fuel in a motor and utilizing the products of combustion as a source of power.

This invention in general relates to improved thixotropic emulsions.

In the following copending patent applications: S.N. 286,877 filed May 20, 1963 (relating to certain unique thixotropic emulsions) now abandoned; S.N. 302,001, filed Aug. 14, 1963 (relating in general to certain unique thixotropic hydrazine emulsions) issued as U.S. Patent No. 3,396,537 on Aug. 13, 1968; S.N. 302,177, filed Aug. 14, 1963 (relating to certain unique thixotropic jet and rocket fuel emulsions) now abandoned; and S.N. 411,103 filed Nov. 13, 1964 (relating to processes of continually preparing these unique emulsions) now abandoned; there are disclosed certain thixotropic emulsions and systems relating thereto. These patent applications are, by reference, incorporated into the present application as if part hereof.

The advantages of the emulsified fuels described in the above patent applications have been demonstrated. Among other things, it has been found that when liquid fuels are subjected to crashes or military action or exposed to firearms or other means of ignition under fire power, serious fires and explosions often result. However, when emulsified fuels are subjected to crashes or to firearms or other fire power, the danger from serious fires and explosions is substantially reduced or eliminated.

The unique thixotropic emulsions described herein have been amply described in the above patent applications. It should be noted that these emulsions can be prepared by any suitable emulsifying agent. Although oxyalkylates are preferred, other types of suitable emulsifiers can also be employed.

By using the means of selecting suitable emulsifiers described in the above applications, one can select and employ emulsifiers, for example, of the following types:

(I) ANIONIC

(A) Carboxylic acids:

- (1) Carboxyl joined directly to the hydrophobic group (subclassification on basis of the hydrophobic group), e.g., fatty acids, soaps, rosin soaps, etc.
- (2) Carboxyl joined through an intermediate linkage.
 - (a) Amide group as intermediate link.
 - (b) Ester group as intermediate link.
 - (c) Sulfonamide group as intermediate link.

2

(d) Miscellaneous intermediate links, ether, —SO₂—, —S—, etc.

(B) Sulfuric esters (sulfates):

- (1) Sulfate joined directly to hydrophobic group.
 - (a) Hydrophobic group contains no other polar structures (sulfated alcohol and sulfated olefin type).
 - (b) Sulfuric esters with hydrophobic groups containing other polar structures (sulfated oil type).
- (2) Sulfate group joined through intermediate linkage.
 - (a) Ester linkage (Artic Syntex M. type).
 - (b) Amide linkage (Xynomine type).
 - (c) Ether linkage (Triton 770 type).
 - (d) Miscellaneous linkages (e.g., oxyalkylimidazole sulfates).

(C) Alkane sulfonic acids:

- (1) Sulfonic group directly linked
 - (a) Hydrophobic group bears other polar substituents ("highly sulfated oil" type). Chloro, hydroxy, acetoxy, and olefin sulfonic acids (Nytron type).
 - (b) Unsubstituted alkane sulfonic acids (MP 189 type; also cetane sulfo acid type).
 - (c) Miscellaneous sulfonic acids of uncertain structure, e.g., oxidation products of sulfurized olefins, sulfonated rosin, etc.
- (2) Sulfonic groups joined through intermediate linkage.
 - (a) Ester linkage.
 - (1) RCOO X-SO₃H (Igepon AP type).
 - (2) ROOC-X-SO₃H (Aerosol and sulfacetate type).
 - (b) Amide linkage.
 - (1) RCONH-X-SO₃H (Igepon T type).
 - (2) RNHOC - X - SO₃H (sulfosuccinamide type).
 - (c) Ether linkage (Triton 720 type).
 - (d) Miscellaneous linkages and two or more linkages.

(D) Alkyl aromatic sulfonic acids:

- (1) Hydrophobic group joined directly to sulfonated aromatic nucleus (subclasses on basis of nature of hydrophobic group. Alkyl phenols, terpene, and rosin-aromatic condensates, alkyl aromatic ketones, etc.).
- (2) Hydrophobic group joined to sulfonated aromatic nucleus through an intermediate linkage.
 - (a) Ester linkage (sulfophthalates, sulfobenzoates).
 - (b) Amide and imide linkages.
 - (1) R-CONH-ArSO₃H type.
 - (2) Sulfobenzamide type.
 - (c) Ether linkage (alkyl phenyl ether type).
 - (d) Heterocyclic linkage (Ultravon type, etc.).
 - (e) Miscellaneous and two or more links.

(E) Miscellaneous anionic hydrophilic groups:

- (1) Phosphates and phosphonic acids.
- (2) Persulfates, thiosulfates, etc.
- (3) Sulfonamides.
- (4) Sulfamic acids, etc.

(II) CATIONIC

(A) Amine salts (primary, secondary, and tertiary amines):

- (1) Amino group joined directly to hydrophobic group.
 - (a) Aliphatic and aromatic amino groups.
 - (b) Amino group is part of a heterocycle (alkaterge type).

- (2) Amino group joined through an intermediate link.
- Ester link.
 - Amide link.
 - Ether link.
 - Miscellaneous links.
- (B) Quaternary ammonium compounds:
- Nitrogen joined directly to hydrophilic group.
 - Nitrogen joined through an intermediate link.
 - Ester link.
 - Amide link.
 - Ether link.
 - Miscellaneous links.
- (C) Other nitrogenous bases:
- Non-quaternary bases (classified as guanidine, thiuronium salts, etc.).
 - Quaternary bases.
- (D) Non-nitrogenous bases.
- Phosphonium compounds.
 - Sulfonium compounds, etc.

(III) NON-IONIC

- Ether linkage to solubilizing groups.
- Ester linkage.
- Amide linkage.
- Miscellaneous linkages.
- Multiple linkages.

(IV) AMPHOLYTIC

- Amino and carboxy:
 - Non-quaternary.
 - Quaternary.
- Amino and sulfuric ester:
 - Non-quaternary.
 - Quaternary.
- Amine and alkane sulfonic acid.
- Amine and aromatic sulfonic acid.
- Miscellaneous combinations of basic and acidic groups.

In employing these thixotropic emulsions, certain problems are often encountered. For example, the lower limit of the temperature stability of these emulsions is usually the freezing point of the external phase. Thus, where emulsified fuels are employed and subjected to temperatures below freezing, it is desirable to incorporate therein certain antifreeze additives, for example, alcohols, ketones, glycols, etc. such as methyl alcohol, ethyl alcohol, etc., alkylene glycols, such as ethylene glycol, diethylene glycol, etc., ketones such as acetone, etc.

I have unexpectedly found that large amounts of water can be replaced with anti-freeze compounds without affecting the stability or rheological properties of the emulsions. For example, 50% or more of the water can be replaced by methyl alcohol, ethylene glycol, etc., without affecting its properties. The amount of anti-freeze additive employed can vary widely depending on the additive of the system, the temperature of operation, etc., 1% or more of the water, for example from 5-75% of the water, such as from 10 to 70%, but preferably from 25 to 60%.

It should be noted that when anti-freeze compounds are employed, despite the fact that extremely small percentages of water are present, one unexpectedly obtains excellent emulsions so that the non-combustible part of the emulsion is extremely small. Thus, most of the emulsion is combusted during burning.

The presence of water in the fuel poses certain problems in respect to corrosion, particularly as to ferrous metals. Thus, it is advantageous to employ a corrosion inhibitor which is soluble in either or both the oily or the non-oily phase. Thus, oil-soluble and/or water soluble corrosion inhibitors can be employed.

I have found that problems in corrosion can be solved by the addition of suitable corrosion inhibitors. Any suitable corrosion inhibitor can be employed, for example, those of the film-forming or the non-film-forming type. In

practice, the film-forming type of corrosion inhibitor is preferred in most instances and therefore it will be more fully discussed.

In general, film-forming organic corrosion inhibitors are generally heteropolar, for example, cationic or anionic in nature. The most widely used type of film-forming corrosion inhibitor is the cationic type, which is generally a comparatively high molar organic compound containing one or more basic nitrogen atoms.

Anionic film-forming inhibitors contain hydrophobic groups, which have generally large hydrocarbon radicals, and acid groups. In general, they are used as the free acid or as salts thereof, for example as alkali or alkaline earth metal, ammonium or amine, etc. salts, for example as the sodium, potassium, calcium, ammonia, amine, etc. salts.

In general, assuming a monomolecular layer, the more effective film-forming corrosion inhibitors are those which cover the largest area per molecule and form the most coherent and oriented film.

Typical, but non-limiting examples, of film-forming corrosion inhibitors are presented below.

NITROGEN BASES

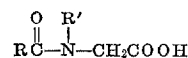
A wide variety of these compounds are known to be film-forming corrosion inhibitors. The following are a few non-limiting examples:

- Oxazolines (U.S. Patent 2,587,955)
- Tetrahydropyrimides (U.S. Patent 2,640,029)
- Imidazolines (Re. 23,227)
- Pyrrrolinedinone (U.S. Patent 2,466,530)
- Amino amides (U.S. Patents 2,550,582 and 2,598,213)
- Quaternary amines (U.S. Patent 2,659,693)
- Monoamines, such as Rosin Amine (Oil Gas Journal 46, No. 31, 91-6 (1946)), Oxyalkylated Rosin Amine (U.S. Patent 2,564,749), Rosin Amine+solubilizing agent (U.S. Patents 2,564,757 and 2,564,753).

CARBOXYLIC ACIDS

A wide variety of these compounds are known to be film-forming corrosion inhibitors. The following are non-limiting examples:

- Naphthenic acids (U.S. Patents 2,430,951 and 2,434,978)
- Dimerized unsaturated fatty acids (U.S. Patent 2,632,695)
- Fatty acids, such as ricinoleic acid (U.S. Patents 2,481,372 and 2,507,401)
- Alkenyl succinic acids (British Patent 576,089)
- Alkenyl succinic acid amine reaction products (U.S. Patents 2,604,451, 2,568,876, 2,540,800, 2,638,449, 2,638,450, and 2,682,489)
- Phthalamic acids (U.S. Patent 2,408,102)
- Monoesters and amides of dicarboxylic acids (U.S. Patent 2,408,102)
- Acid-esters, for example, sorbitan monooleate and fatty acid partial esters of pentaerythritol (U.S. Patents 2,479,424 and 2,574,954)
- Sorbitan and pentaerythritol (U.S. Patent 2,580,036) Acid-ester and amine salts of fatty acids (U.S. Patents 2,564,422 and 2,564,423)
- Acids from oxidized paraffin wax
- Dimerized and polymerized unsaturated fatty acids (U.S. Patents 2,632,709, 2,627,474, 2,631,979)
- Amides of amino acids such as the sarcosines for example



R=fatty hydrocarbon group
R'=H, lower alkyl

5 SULFONIC ACIDS

A wide variety of these compounds are known to be film-forming corrosion inhibitors. The following are a few non-limiting examples:

- (1) Mahogany sulfonates and salts thereof (U.S. Patents 2,533,301, 2,533,302, 2,533,303, 2,533,304, 2,594,266, 2,511,250, 2,598,725, 2,499,710, 2,509,786, 2,582,733)
- (2) Synthetic alkyl aryl-sulfonates (U.S. Patents 2,562,845 and 2,546,552)

MISCELLANEOUS CORROSION INHIBITORS

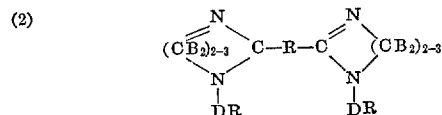
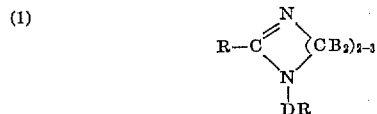
A wide variety of other compounds are known to be film-forming corrosion inhibitors. The following are a few non-limiting examples:

- (1) Acid-esters of phosphoric and thiophosphoric acids.
- (2) Substituted ureas and thioureas.
- (3) Propargyl compounds, for example propargyl alcohol, sulfide, etc.

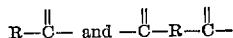
These corrosion inhibitors are employed in concentrations which are effective for that particular system.

The imidazolines are a member of the cyclic amidine family of compounds and are prepared in the manner described in Reissue 23,227, U.S. Patent 2,468,163, and elsewhere.

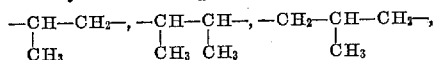
They may be described, for example, as follows:



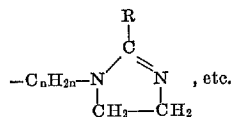
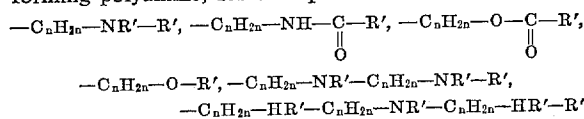
where



are residues derived from the carboxylic acid employed in preparing the compound wherein R is, for example, a hydrocarbon radical, having, for example, up to about 30 carbon atoms, such as 1-30 carbon atoms, B is hydrogen or a hydrocarbon radical, for example, a lower alkyl, such as methyl—for example, where CB₂ is

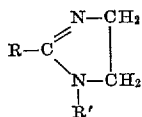


but preferably $-\text{CH}_2-\text{CH}_2-$ or $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, and R is the residue derived from the cyclic amidine-forming polyamine, for example where DR is



and wherein n is, for example, the numeral 1 to 6 and R' is hydrogen or an aliphatic, cycloaliphatic hydrocarbon, etc., radical.

In the simplest case, the group R' may be directly attached to the 1-nitrogen atom of the ring, as follows:

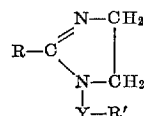


The particularly outstanding corrosion-preventive reagents result when the cyclic amidine contains basic nitrogen groups in addition to those inherently present in the

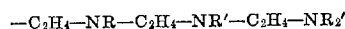
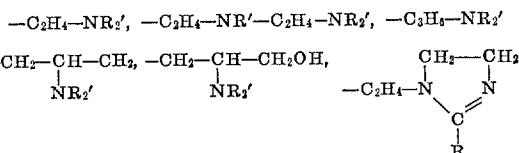
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imidazoline ring. In general, compounds of this type which are effective are those in which the basic nitrogen group is contained in the radical D in the above formula.

In this case the products may be represented by the formula

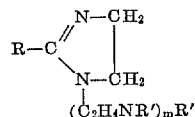


where R and R' are hydrogen or a hydrocarbon radical, and in which at least one of the groups R and R' is an aliphatic or cycloaliphatic hydrocarbon group containing from 8 to 32 carbon atoms; and Y is a divalent organic radical containing amino groups. The group R' may be, and usually is, an amino nitrogen substituent. Examples of organic radicals which Y—R' may represent are



where R' and R have their previous significance.

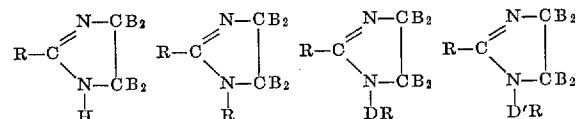
Of this class of reagents in which an amino group occurs as a portion of the 1-nitrogen substituent, those which are derived, at least theoretically, from the polyethylene polyamines appear to be particularly effective as corrosion inhibitors. These have the general formula



where R and R' have their previous meanings, and m is a small number, usually less than 6. Amides of these imidazolines are also effective.

Imidazolines have been described in Re. 23,227. A typical claim is as follows:

"A process for preventing corrosion of metals, comprising the step of applying to such metals a substituted imidazoline selected from the class consisting of



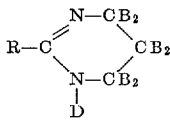
in which D represents a divalent, non-amino organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O, and N; D' represents a divalent, organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O and N; D' represents a divalent organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O and N, and containing at least one amino group; R is a member of the class consisting of hydrogen and aliphatic and cycloaliphatic hydrocarbon radicals; with the proviso that at least one occurrence of R contains 8 to 32 carbon atoms; and B is a member of the class consisting of hydrogen and alkyl radicals having not over 2 carbon atoms, with the proviso that at least three occurrences of B be hydrogen."

Tetrahydropyrimidines have been described in U.S. Patent 2,640,028 where a typical claim is as follows:

"A process for preventing corrosion of metals includ-

7

ing the step of applying to such metals a substituted tetrahydropyrimidine of the formula type:



where D is a member of the class consisting of D'—R and R' D' represents a divalent organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O and N; R is a member of the class consisting of hydrogen and hydrocarbon radicals, with the proviso that at least one occurrence of R contains from 8 to 32 carbon atoms; B is a member of the class consisting of hydrogen and hydrocarbon radicals containing less than 7 carbon atoms, with the proviso that at least three occurrences of B be hydrogen."

In general, the preferred embodiments of film-forming corrosion inhibitors are of the type of cyclic amidines described above and acylated alkylene polyamines of the type described in U.S. Patent 2,598,213 which are by reference incorporated in the present application.

The amount of corrosion inhibitor employed herein can vary widely depending on the particular system, the particular corrosion inhibitor, the conditions under which it is employed, etc. The amount of corrosion inhibitor can range, for example, from about 1 p.p.m. or more, such as from about 5–50,000 or more p.p.m., for example from about 5–10,000 p.p.m. but preferably from about 10 to 1,000 p.p.m.

Other problems are also encountered in fuel systems. For example, hydrocarbon emulsion systems are subjected to the growth of bacteria, algae and other biological systems which results, among other things, in increased corrosion and in the plugging of lines and filter elements.

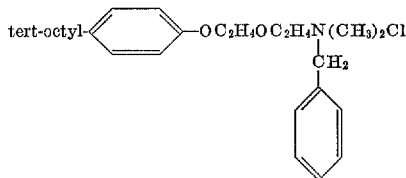
I have discovered that biocides which are capable of reducing such growth can be incorporated into the emulsions in sufficient amounts to afford biocidal protection, for example, in amounts of about 0.1–20,000 or more parts per million (p.p.m.) of emulsion, such as about 0.5–10,000 p.p.m. such as 10–1,000 p.p.m. but preferably 1–500 p.p.m. Of course, the optimum amount will depend on many factors such as the particular system, the particular additive, etc.

The following are non-limiting representative examples of biocidal agents.

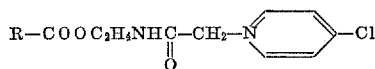
In general, quaternary amino compounds are employed in the preferred embodiment of my invention. The following is a list of quaternary biocides.

(1) The coco-dimethyl benzyl ammonium chloride type which is also referred to as benzalkonium chloride, for example those sold under the Zephiran, Roccal, BTC Ammonyx T and Bional trademarks.

(2) Hyamine 1622 (Rohm & Haas Co.) type for example



(3) Emulsept (Emulsol Corp.) type, for example



frequently referred to as N(acylcolaminoformylmethyl) pyridinium chloride.

(4) Lauryl and other long-chain alkylpyridinium chlorides.

8

(5) Octadecenyldimethylethylammonium chloride and the corresponding trimethyl compound, as well as the bromide salts of these cations.

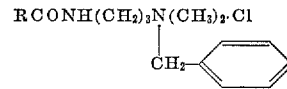
(6) Cetyltrimethylammonium bromide, widely used in Great Britain under the names Cetab and Cetavlon as well as the corresponding dimethylethyl and dimethylbenzyl derivatives.

(7) Alkylisoquinolinium halides.

(8) Alkyldimethyl-3,4-dichlorobenzylammonium chlorides and corresponding diacyl monomethyl compounds.

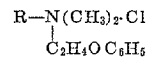
(9) Alkyl-gamma-picolinium halides.

(10)

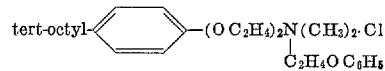


and its analogs.

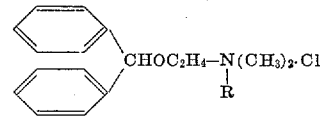
(11) Quaternary ammonium compounds in which the N atom bears the usual long chain and also a phenoxyethyl groups; the typical structure is



The phenoxyethyl group has also been used as a nitrogen substituent in compounds of the Hyamine type.

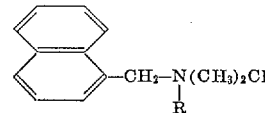


(12) Compounds in which the benzhydryl ether group is used, a nitrogen substituent such as

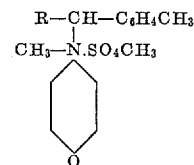


where R is a C₈ to C₁₂ straight-chain alkyl group.

(13) The α-menaphthyl type for example

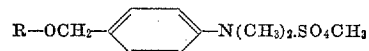


(14) Alpha-substituted benzylamines quaternized with cyclic or acyclic substituents, for example



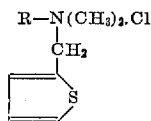
where R has the usual significance. The morpholinium ring may be replaced by a piperidine ring.

(15) Aromatic amines substituted by an alkoxyethyl group.



This compound is made by reacting dimethylaniline with formaldehyde and converting the resulting p-dimethylaminobenzyl alcohol to its dodecyl ether via sodium and dodecyl bromide. It is then quaternized with methyl sulfate.

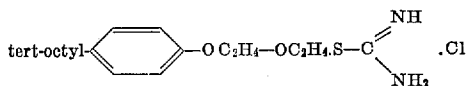
(16) Quaternary nitrogen compounds in which one of the N-substituents is a thienyl group.



(17) Bis-quaternary compounds prepared by adding 2 moles of a tertiary amine to butadiene bis-chlorohydrin.

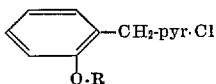
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(18) The thionium analogs of the Hyamine 1622 type for example

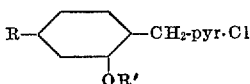


(19) Quaternized picolinic acid esters of long-chain fatty alcohols. The quaternizing agent is methyl sulfate or methyl p-toluenesulfonate.

(20) Alkoxybenzylpyridinium chlorides



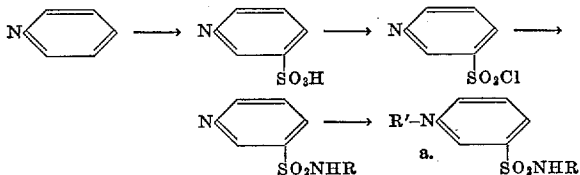
and the analogous



where R' is a short alkyl group.

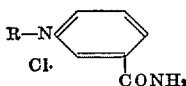
(21) Bis - quaternary compounds prepared from 2 moles of $\text{RN}(\text{CH}_3)_2$ and 1 mole of a xylene dihalide.

(22) Quaternized pyridinesulfonamides, prepared by the following series of reactions

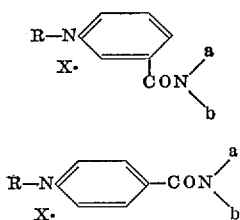


where R is a long alkyl chain, R' is a short alkyl group such as methyl, and a is an anion such as Cl^- , Br^- , SO_3CH_3^- , etc.

(23) N-alkylnicotinamides



and the analogous series

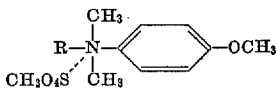


where a and b represent short alkyl groups or a cyclic structure, and X represents a halide ion.

(24) Quinolyloxyalkylammonium halides, corresponding to the phenoxyalkylammonium halides, the key substituents on the N atom being a long alkyl chain and the quinolyloxyalkyl group

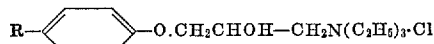


in which the quinoline nucleus is substituted by halogens. (25) o-, m-, and p-dodecylanisidines quaternized with methyl or ethyl sulfate. The cetyl analogs may also be employed.



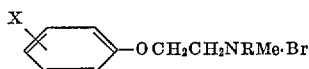
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(26) The phenoxypropyl compounds typified by the products:



5 made by reacting an alkylphenol with epichlorohydrin and triethylamine.

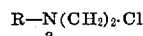
Similar phenoxyethyl compounds:



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where R is an alkyl group containing 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16, or 18 carbon atoms and X is one or two chlorine atoms or isopropyl.

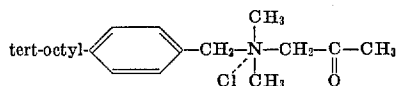
15 (27) Compounds analogous to Cetab, but having one or more of the N-methyl groups replaced by cyclohexyl, hydroxycyclohexyl, or cyclopentenyl groups



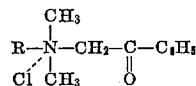
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where a represents an alicyclic group.

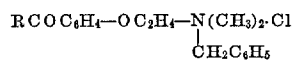
(28) Compounds containing a ketone group in their structure, usually in one of the shorter radicals which is attached to the quaternary nitrogen. Examples are:



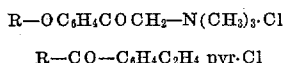
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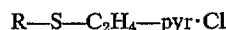
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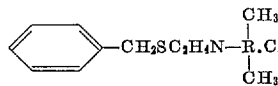


(29) Thioethers of the type:



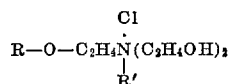
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and



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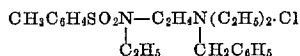
(30) Quaternized ethers of triethanolamine,



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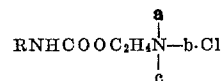
where R' is methyl, ethyl, benzyl, etc.

(31) Sulfonamides containing a quaternary nitrogen



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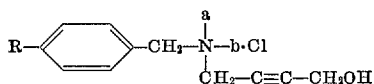
(32) Long-chain carbamates containing a quaternary nitrogen



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where a, b, and c may be short alkyl groups or may form a cyclic structure and an alkyl group.

65 (33) Compounds containing a hydroxybutynyl radical as one of the substituents on the quaternary nitrogen.



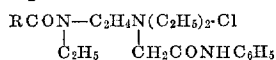
(34) Compounds of the Sapamine type in which one of the substituents on the quaternary nitrogen is the group



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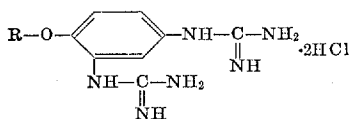
A typical example is



(35) A wide variety of quaternary nitrogen compounds containing two hydrophobic chains



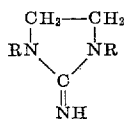
(36) Long-chain guanidine hydrochloride derivatives, such as



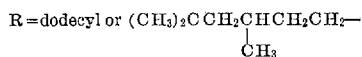
(37) Tetrazoles and tetrazolium compounds.

(38) Benzotriazolium compounds particularly those having dodecyl or hexadecyl group present.

(39) Imidazolium and imidazolium compounds for example 1-decyl-2,3-dimethylimidazole, quaternized with benzyl chloride, the C_{12} to C_{14} derivatives being preferred. $\text{N,N}'$ -dialkyl-2-imino-imidazolines and their salts having the general formula



where



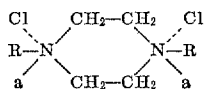
may be employed.

(40) Quaternary nicotinium sulfates prepared by reacting a symmetrical or unsymmetrical dialkyl sulfate containing at least one long-chain group with nicotine.

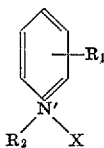
(41) Quaternary compounds made by reacting dodecyl dimethylamine with $\text{R}-\text{CH}_2\text{Cl}$ where R is a benzimidazolyl group or a phenanthridyl group. In this case, the quaternary nitrogen is not part of the heterocycle.

(42) Quaternized derivatives of N-long-chain alkyl 1,2,3,4-tetrahydroquinoline.

(43) Bis-quaternary ammonium compounds made by quaternizing a symmetrical NN' -dialkylpiperazine.



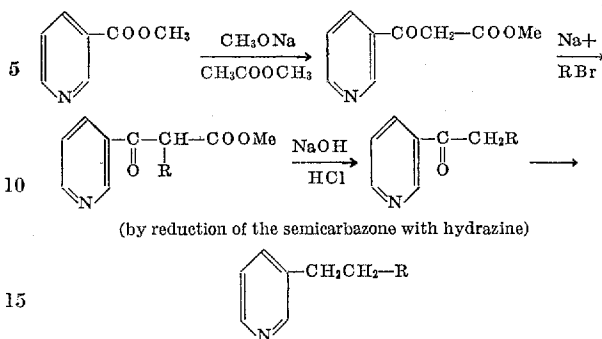
(44) Substituted pyridinium salts having the generic formula



where X is halogen, R_1 and R_2 are alkyl radicals of 1 to 18 carbon atoms and may be the same or different, and where R_1 may occupy the 2-, 3-, or 4-position on the pyridine nucleus. In the preferred final compounds the sum of the carbon atoms in R_1 and R_2 is 17 to 20. The starting point for the synthesis of these compounds

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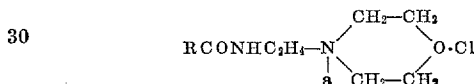
is the appropriate pyridine-carboxylic acid ester, and the reactions are as follows:



The corresponding piperidinium compounds may also be prepared. Higher alkylated pyridones, piperidones, thio-pyridones, and their onium salts may also be employed.

(45) Compounds in which the nitrogen atom of morpholine is the quaternary cationic center, particularly the unsymmetrical dialkyl sulfates, $\text{R}_1\text{SO}_4\text{R}_2$, in which the sum of R_1 and R_2 is in the range of 13 to 32 carbon atoms, as quaternizing agents for alkylmorpholines and other tertiary bases.

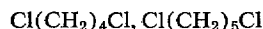
(46) Morpholine derivatives which are closely analogous to the Sapamines having the structure



where a is benzyl may be employed.

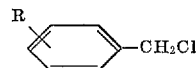
(47) N,N -dialkylmorpholinium chlorides prepared by reacting secondary amines with bis-(2-chloroethyl) ether may be employed. Similar synthesis of N,N -dialkylthiomorpholinium chlorides used mustard gas, bis-(2-chloroethyl) thioether as a starting material.

(48) Long-chain pyrrolidones and pyrrolidinium compounds, and also corresponding piperidinium derivatives from



and higher primary and secondary amines may serve as starting materials.

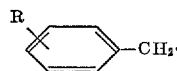
(49) The alkylbenzyl halides of generic formula



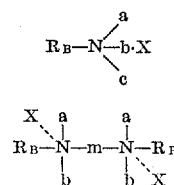
may be employed.

These are prepared by the chloromethylation of alkylbenzenes. These products can be reacted with simple tertiary amines to form quaternary compounds. The alkylbenzyl chlorides can also be reacted with thiourea to form biocidal thuronium salts. They have been used as the long-chain groups in preparing several series of geracidal quaternary ammonium compounds.

If the alkylbenzyl radical



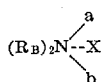
is designated as R_B the following series have been described:



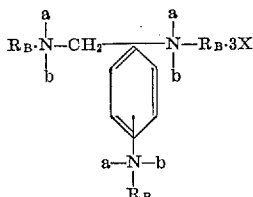
13

where m is a linking group which may contain ether links, amide links, short-chain alkylene links, xylylene links, butynylene or butenylene links.

Bis-compounds of the type



and tris-compounds of the type analogous to the xylylene-linked compounds



may be employed.

(50) Compounds containing chaulmoogryl and hydrocaryl groups may be employed as long chains on pyridinium and dimethylbenzylammonium groups.

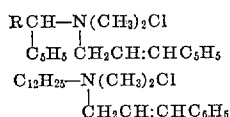
(51) Combinations of a long-chain amine or quaternary ammonium cations with an anion which contributes to the biocidal action may be employed. Among the most widely used cations are the phenolates, particularly pentachlorophenolate. Other cations include those of various polymeric carboxylic acids and of the C_6 to C_{12} alkoxyacetic acids. The naphthenic acid salts of the long-chain quaternaries, and also the salts of phthalic or maleic acid in which one carboxyl is neutralized by a heavy metal and the other carboxyl is neutralized by the quaternary are effective.

(52) Benzoxazine derivatives, formed by reaction an alkylphenol with formaldehyde and a primary amine such as methylamine may be employed.

(53) N - benzyl - N - dodecylspirocyclohexylethyleneammonium bromide and other compounds having the same ring structure may be employed.

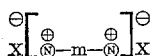
(54) Compounds containing the hydroxycyclooctyl radical, e.g., benzyl dimethyl(2-hydroxycyclooctyl) ammonium bromide and 1-benzyl-1-(2-hydroxycyclooctyl) piperidinium bromide may be employed.

(55) Cinnamyl derivatives such as



may be employed. Many others may also be employed.

In general, I prefer to employ bis-quaternaries, for example those of the general formula

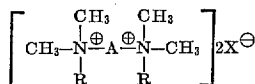


where m is a linking group for example an alkylene, alkynylene, alkenylene, alkaralkylene, alkyleneether-containing, polyalkylene ether-containing, amido-containing, etc. group; X is an anion for example halogen (Cl, Br, etc.), sulfate, sulfate ester, etc.; and \oplus represents a basic group, for example, $\text{RR}'\text{R}''\text{N}$, such as where the R's are alkyl, aralkyl, alkenyl, alkynyl, etc., or where \oplus is part of a cyclic structure for example in piperidine, morpholine, pyridine, quinoline, isoquinoline, picoline, etc.

In addition to the diquaternaries described above, the following are representative examples thereof:

(1) (In application S.N. 149,180.):

Bis-quaternary compounds of the formula

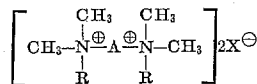


14

where R is an aliphatic hydrocarbon group such as alkyl and alkenyl having at least ten carbon atoms, such as 10-18, but preferably 12-14, with an optimum of 12 carbon atoms; A is an alkylene radical having, for example, from 2-10 or more carbons, but preferably 2-4 carbons; and X is a negative ion, for example, halogen, such as chlorine, bromine, iodine, or sulfate, sulfonate, etc.

(2) (In application S.N. 149,181.):

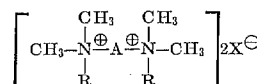
Bis-quaternary compounds of the formula



where R is an aliphatic hydrocarbon group such as alkyl and alkenyl having at least 10 carbon atoms, such as 10-18, but preferably 12-14, with an optimum of 12 carbon atoms, and A is an aralkylene radical having for example from 8-30 or more carbons such as 8-20 carbons but preferably where the aralkylene group is xylylene, and X is a negative ion, for example, a halogen, such as chlorine, bromine, iodine, or sulfate, sulfonate, etc. The aralkylene radical can also be substituted for example with a hydrocarbon, a halogen, a hydroxy, etc.

(3) (In application S.N. 149,182.):

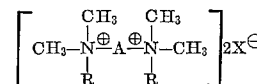
Bis-quaternary compounds of the formula:



where R is an aliphatic hydrocarbon group such as alkyl and alkenyl having at least 10 carbon atoms, such as 10-18, but preferably 12-14, with an optimum of 12 carbon atoms, and A is an unsaturated aliphatic hydrocarbon radical having for example from 2-10 or more carbons but preferably 4 carbons for example alkenylene and alkynylene radicals and X is a negative ion, for example, a halogen, such as chlorine, bromine, iodine, or sulfate, sulfonate, etc.

(4) (In application S.N. 149,228.):

Bis-quaternary compounds of the formula



where R is an aliphatic hydrocarbon group such as alkyl and alkenyl having at least 10 carbon atoms, such as 10-18, but preferably 12-14, with an optimum of 12 carbon atoms, and A is an alkylene ether radical including cycloalkylene ether radicals having for example from 1-10 or more carbons such as 1-4 but preferably 2 carbons in each alkylene unit and X is a negative ion, for example, a halogen, such as chlorine, bromine, iodine, or sulfate, sulfonate, etc.

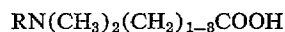
The above patent applications are by reference incorporated into the present application.

This invention has been illustrated with quaternary biocides and in its most preferred embodiment with the diquaternary biocides. For purposes of this invention the ampholytic biocides will be considered to be cationic biocides, for example

(1) $\text{R}_2\text{NR}'\text{NHCH}_2\text{COOH}$ as in the Tego series of biocides for example of the formula



(2) $\text{RR}'\text{R}''\text{N}(\text{CH}_2)_{1-8}\text{COOH}$, for example



where R is a high fatty alkyl, etc.

Other suitable biocides can also be employed.

In addition to the special problems brought about by the emulsion state of the fuel, it is often desirable to

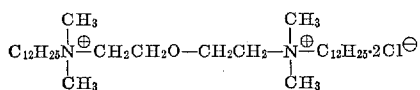
employ other additives to the emulsion, such as for example anti-knock compositions, anti-icing compositions, anti-oxidant compositions, lubricating additives, etc. Illustrative examples of such additives include the following: tetraethyl lead; tricresyl phosphate; "Liquid nickel," and deicers, etc.

In certain instances, it may be desirable to employ a single multi-purpose additive, for example, to employ an additive which acts both as a corrosion inhibitor and a biocide, etc., such as for example diquaternary compounds, etc.

The following examples are presented for purposes of illustration and not of limitation.

Example 1

An emulsion prepared in the manner Example 1 of S.N. 411,103, filed Nov. 13, 1964 was modified by replacing 400 ml. of the 1000 ml. of water in the aqueous phase with ethylene glycol as an anti-freeze compound and adding 100 p.p.m. of a diquaternary compound,



as both a corrosion inhibitor and a biocide.

Thus, the emulsion contains 95% hydrocarbon, 3.46% water, 1.54% antifreeze, 100 p.p.m. of one compound which acts both as a corrosion inhibitor and a biocide.

Since other emulsions were similarly prepared, to save repetitive details, other illustrative emulsions are presented in the following table.

In all of the examples and elsewhere the percentages are by volume and the percentages of water include emulsifiers. Total percentages are based on the sum of the percentages of hydrocarbon, water (including emulsifier) and anti-freeze as 100%.

It is to be noted that the percentages of water (including emulsifier) are extremely small, i.e. 1-2%. The anti-freeze compounds enhance the emulsion in that the non-combustible fraction, i.e. water, is minimized without detracting from the properties of the emulsion since the anti-freeze compounds and emulsifiers are combustible. Thus, the anti-freeze compounds, in essence, are more than an anti-freeze compound. They are also combustion enhancers, in that they reduce the non-combustible moiety of the emulsion without decreasing its suitability.

In practice, one attempts to employ as much hydrocarbon as possible and as little of the other components and additives as possible consistent with obtaining optimum emulsion properties. Thus, in preparing the emulsion one generally attempts to employ as high a percentage of hydrocarbon as possible, i.e., 95% or greater, preferably 97% or greater, but preferably 98% or greater, approaching 99+% hydrocarbon. This is achieved by employing the anti-freeze compound.

Thus, examples of emulsions include those in the following ranges:

TABLE II

	Broad range	Intermediate range	Optimum range
Hydrocarbon, percent.....	70-99.5	80-99	90-99
Water, percent.....	0.5-30	0.5-20	0.75-10
Anti-Freeze Compound, percent.....	0.25-20	0.25-15	0.5-7
Corrosion Inhibitor ¹ (p.p.m.).....	1-50,000	5-10,000	10-1,000
Biocide ¹ (p.p.m.).....	0.1-20,000	0.5-10,000	1-500

¹ Note the corrosion inhibitor and biocide may constitute the same compound.

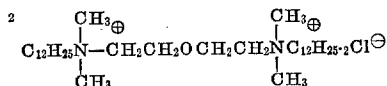
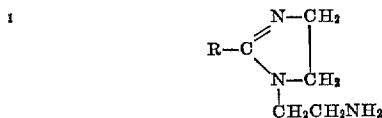
As is quite evident, new additives including corrosion inhibitors, anti-freeze compounds, biocides, etc. will be constantly developed which could be useful in this invention. It is, therefore, not only impossible to attempt a comprehensive catalogue of such additives, but to attempt to describe the invention in its broader aspects in terms of specific chemical names used would be too voluminous and unnecessary since one skilled in the art could by following the description of the invention herein select a useful additive. This invention lies in the use of a suitable additive and its individual composition is important only in the sense that its properties can affect its proper function. To precisely define each specific useful additive in light of the present disclosure would merely call for knowledge within the skill of the art in a manner analogous to a mechanical engineer who prescribes in the construction of a machine the proper materials and the proper dimensions thereof. From the description in this specification and with the knowledge of one skilled in the art one will know or deduce with confidence the applicability or a specific additive suitable for this invention by applying them herein. In analogy to the case of a machine, wherein the use of certain materials of construction or dimensions of parts would lead to no practical useful result, various materials will be rejected as inapplicable where others would be operative. One would obviously assume that no one will wish to use a useless additive nor will be misled because it is possible to misapply the teachings of the present disclosure to do so. Thus, any additive that can perform the functions stated herein can be employed.

Having thus described my invention what I claim as new and desire to obtain by Letters Patent is:

1. A thixotropic hydrocarbon-in-water emulsion fuel comprising (1) water, (2) an emulsifiable hydrocarbon, (3) an emulsifying agent, and (4) an additive selected from the group consisting of corrosion inhibitor additives, anti-freeze additives, biocidal protective additives, anti-knock compositions, anti-icing compositions, anti-oxidant compositions, lubricating additives, multi-purpose additives having at least two of the properties of said respective additives and compositions, and mixtures of

TABLE I

Ex.	Hydrocarbon		Anti-Freeze Compound		Corrosion Inhibitor		Biocide		Other additions, type
	Type	Percent	Water percent	Type	Percent	Type	P.p.m.	Type	
2	JP-4	97.5	1.50	Ethylglycol.	1.00	Imidazoline ¹	100		
3	Gasoline	98.0	1.75	Methanol	0.25				Tetraethyl lead, commercial amounts.
4	do	97.8	1.20	Ethylene glycol.	1.00			Diquaternary ²	100
5	do	97.8	1.20	do	1.00			Diquaternary ²	100
6	JP-4	98.2	1.25	do	0.55	Diquaternary ²	200		TCP, commercial amounts, Phillips anticler, commercial amounts.



acts as both a corrosion inhibitor and a biocide.

at least two of said additives and compositions, said hydrocarbon being present in said emulsion fuel in an amount of at least 80% hydrocarbon by volume of the emulsion, said emulsion having the characteristics of a solid fuel when at rest and the characteristics of a liquid fuel when a force is exerted on it, said emulsion tending to be non-adhesive, said emulsion having a critical shear point sufficient to permit pumping at high rates, and said emulsion having an apparent rest viscosity greater than about 1000 cps.

2. The thixotropic hydrocarbon-in-water emulsion fuel of claim 1 wherein the additive is an anti-freeze additive.

3. The thixotropic hydrocarbon-in-water emulsion fuel of claim 1 wherein the additive is a corrosion inhibitor additive.

4. The thixotropic hydrocarbon-in-water emulsion fuel of claim 1 wherein the additive is a biocidal protective additive.

5. The thixotropic hydrocarbon-in-water emulsion fuel of claim 1 wherein the additive is a mixture of an anti-freeze additive, a corrosion inhibitor additive, and a biocidal protective additive.

6. The method of providing power comprising burning the fuel of claim 1 in a motor and utilizing the products of combustion as a source of power.

7. The method of providing power comprising burning the fuel of claim 2 in a motor and utilizing the products of combustion as a source of power.

8. The method of providing power comprising burning the fuel of claim 3 in a motor and utilizing the products of combustion as a source of power.

9. The method of providing power comprising burning the fuel of claim 4 in a motor and utilizing the products of combustion as a source of power.

10. The method of providing power comprising burning the fuel of claim 5 in a motor and utilizing the products of combustion as a source of power.

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BENJAMIN R. PADGETT, Primary Examiner

U.S. Cl. X.R.

44-7, 51; 149-109