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GASOLINE INHIBITED AGAINST EMULSION FORMATION

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ABSTRACT OF THE DISCLOSURE

This invention is directed to a gasoline to which has been added certain chemicals to prevent emulsion formation. The chemicals used to treat the gasoline are lower aliphatic polycarboxylic acids used alone or in combination with nonionic surface active agents.

INNTRODUCTION

Motor fuels boiling within the gasoline range are frequently treated with a variety of additives to improve their operating performance when used as fuels for internal combustion engines and to improve their storage characteristics. Typical gasoline fuels in addition to the base fuel contain such additives as lead anti-knock compounds, anti-oxidants, gum inhibitors, corrosion inhibitors, and additives to prevent carburetor icing.

In certain cases these additives are surface active agents which promote the emulsification tendencies of gasoline motor fuels with water. When such emulsions form they render the gasoline unsuitable for use as a motor fuel.

The most common offender from the standpoint of promoting water-in-gasoline emulsions are polar organic corrosion inhibitors such as fatty amine carboxylic acid salts. Also offensive as emulsion promotors are the carburetor icing preventatives which are frequently either amines or amine salts. Illustrative of the anti-icing additives are the fatty imidazoline salts disclosed in Bott, U.S. 3,257,179. These additives are sometimes present in gasoline fuels in amounts ranging up to 2% by weight.

With the increased tendencies of gasolines to form emulsions with water it would benefit the art to add to such gasolines chemical compositions which would prevent the formation of such emulsions so that the gasoline is suitable for use as a fuel in internal combustion engines.

OBJECTS OF THE INVENTION

Based on the above it is, therefore, an object of the invention to provide gasoline which contains an additive whereby the tendency of such gasoline to form emulsions with water are inhibited.

A specific object of the invention is to provide a gasoline which contains minor amounts, e.g., up to 2% by weight of polar organic compounds capable of preventing the corrosive and carburetor icing tendencies of said gasoline, which also contains an emulsion preventative amount of certain chemicals.

Other objects will appear hereinafter.

THE INVENTION

In accordance with the invention it has been found that an improved motor fuel for internal combustion engines is provided by utilizing a major portion of gasoline which contains not more than 2% by weight of polar organic compounds capable of preventing the corrosive and carburetor icing tendencies of said gasoline and from 0.1 to 15 p.p.m. of an aliphatic polycarboxylic acid from the group consisting of diglycollic acid, citric acid, fumaric acid and adipic acid.

In a preferred embodiment of the invention the above described acids are combined in a weight ratio of from 10:1 to 10:3 with a non-ionic wetting agent.

The preferred aliphatic polycarboxylic acids used in the practices of the invention are diglycollic acid and citric acid.

The non-ionic wetting agents most preferred in practicing the invention are certain phenol-formaldehyde condensation products and certain glycol esters, which in a preferred embodiment are combined in a weight ratio of from 1:6 to 6:1.

THE NON-IONIC SURFACE ACTIVE AGENTS

The non-ionic surface active agents may be selected from a broad class of well-known materials. They preferably contain varying amounts of alkoxy groups, particularly ethoxy or propoxy groups or mixtures thereof. They are most desirable soluble at use concentrations in the gasoline to be treated.

The preferred non-ionic surface acting agents are certain phenol-formaldehyde condensation products.

PHENOL-FORMALDEHYDE CONDENSATION

The phenol-formaldehyde condensation products are prepared by reacting formaldehyde or a substance which breaks down to formaldehyde under the reaction conditions, e.g., paraformaldehyde and trioxane, and a difunctional, monoalkyl phenol, such as a substantially pure ortho- or para-monoalkyl phenol or a crude alkyl phenol consisting of at least 75% difunctional phenol by heating the reactants in the presence of a small amount of acid catalysts such as sulfamic acid. The aqueous distillate which begins to form is collected and removed from the reaction mixture. After several hours of heating at temperatures slightly above the boiling point of water, the mass becomes viscous and is permitted to cool to about 100 to 105° C. At this point a suitable hydrocarbon fraction is added, and heating is resumed. Further aqueous distillate begins to form and heating is continued for an additional number of hours until at least about one mol of aqueous distillate per mol of reactants has been secured. The product is permitted to cool to yield the phenol-formaldehyde condensation product in a hydrocarbon solvent. The molecular weight of these intermediate condensation products cannot be ascertained with certainty, but we would approximate that they contain about 3 to 15 phenolic nuclei per resin molecule. The solubility of the condensation product in hydrocarbon solvents such as SO_2 extract would indicate that the resin is a linear type polymer, thus distinguishing them from the more common phenol-formaldehyde resins of the cross-linked type.

The phenol component of our phenol-formaldehyde resins is entirely or principally a difunctional phenol-one having only two of the three normally reactive ortho- and para-positions available for reaction with the formaldehyde. These phenols are mono-alkyl phenols with the alkyl group in the para- or ortho-position having up to about 15 carbons. Phenols suitable for our invention are difunctional, mono-alkyl phenols having straight chain or branch chain alkyl groups of 4–15 carbons, preferably 5–15 carbons. Examples of the phenolic component include such preferred phenols as p-tertiary butyl phenol, p-tertiary hexyl phenol, p-tertiary octyl (1,1,3,3-tetramethyl butyl-1) phenol, p-nonyl phenol, p-dodecyl phenol, a crude alkyl phenol containing about 90% p-nonyl phenol and 10% dinonyl phenol, and others including mixtures of ortho- and/or para-monoalkyl phenols and crude alkylate phenols containing at least 75% difunctional alkyl phenols with the remainder being primarily monofunctional phenols.

It is also possible to use mixtures of monoalkyl phenols having 4–15 carbons or even mixtures wherein one alkyl phenolic compound of the mixture has an alkyl group of less than 4 carbons, e.g. n-propyl or isopropyl, so long as there is sufficient alkyl phenol having more than 4

carbons in the alkyl group in the mixture to make an average of at least 4 carbons in the alkyl group.

The intermediate phenol-formaldehyde condensation products used in preparing the compositions of this invention and methods of their preparation are illustrated in the following examples. All parts are by weight unless otherwise designated.

Example A

In a three-necked reaction flask provided with means of mechanical stirring and a return condenser system permitting the removal of any aqueous phase formed in the course of reaction, there is added 1500 parts of a crude alkylate phenol which comprises an undistilled p-nonyl phenol containing approximately 10% of dinonylphenol, 225 parts paraformaldehyde and 3 parts sulfamic acid which is present as a catalyst in the reaction. The reaction mass is heated, and at 108° C. an aqueous distillate begins to form. After three hours heating at approximately 110° C., the mass becomes quite viscous and is permitted to cool to about 100° C. At this point 600 parts of SO_2 extract is added and heating resumed. Again at 110° C. further aqueous distillate begins to form and heating is continued for an additional three hours, or until approximately 141 cc. of aqueous distillate has been secured at a maximum temperature of 212° C. The product is permitted to cool to yield the finished phenolformaldehyde condensation product.

Example B

In a manner similar to Example A, 1000 parts of the crude alkylate phenol, 120 parts of paraformaldehyde and 2 parts sulfamic acid were heated 2 hours at 105–110° C. to permit reaction of the phenol and formaldehyde under conditions minimizing formaldehyde loss. At temperatures above 110° C. vigorous reaction sets in which must be controlled by cooling. After about 27 parts of aqueous distillate have been secured, the reaction comes under control and becomes exceedingly viscous. At this point the resin is cooled to 105° C., and 400 parts of SO_2 extract is added. Heating is continued for an additional three hours or until a total of about 75 parts of aqueous distillate have been removed at maximum temperature of 212° C. to yield the finished phenol-formaldehyde condensation product.

Example C

In a manner similar to Examples A and B, 1000 parts of the crude alkylate phenol, 90 parts paraformaldehyde and 2 parts sulfamic acid are carefully reacted at temperatures of 100–110° C. When the reaction mass becomes quite viscous, the reaction is permitted to cool, and 400 parts of SO_2 extract is added and heating resumed for an additional hour or until a total of 55 parts of aqueous distillate have been secured at maximum temperature of 213° C.

Example D

To a vessel having a stirrer and a return condenser system permitting the removal of the aqueous phase of the distillate is added 1400 parts of p-tertiary butyl phenol, 310 parts of paraformaldehyde and 3 parts of sulfamic acid as catalyst. The mass is heated, at about 105–110° C. an aqueous distillate begins to form. After heating for three hours at 105–110° C., the mass becomes viscous and is permitted to cool to 95–110° C. About 500 parts of a suitable hydorcarbon fraction is added and heating is resumed. At 105–110° C., further distillate begins to form and heating is continued for an additional three hours until approximately 140 cc. of aqueous distillate is obtained. The product is cooled to yield the phenolformaldehyde resin solution in the hydrocarbon vehicle.

Example E

Following the technique of Example D, an equivalent amount of p-tertiary hexyl phenol is substituted for the p-tertiary butyl phenol of Example D.

In the preceding examples, sulfamic acid has been used as the acid catalyst to assist in the condensation reaction. Other suitable equivalent acids which may be used in place of sulfamic acid are mineral acids such as sulfuric acid, hydrochloric acid, phosphoric acid, etc.

As stated heretofore, intermediate phenol-formaldehyde resin should contain a minimum of about 4-phenolic nuclei and should not exceed about 15 phenolic nuclei. It is extremely difficult, if not impossible, to accurately determine the molecular weight of the intermediate resin products. However, it is believed that the resin of Example A contains about 10 phenolic nuclei per resin molecule, Example B, about 7 phenolic nuclei, and Example C, about 4 phenolic nuclei per resin molecule.

OXYALKYLATIONS OF PHENOL FORMALDEHYDE CONDENSATION PRODUCTS

The condensation products used in the practice of the invention may be oxyalkylated with ethylene oxide, propylene oxide-1,2 or both oxides.

OXYALKYLATION OF THE CONDENSATION PRODUCTS

Having prepared the intermediate phenol-formaldehyde products, the next step is the oxyalkylation of the condensation products at the —OH group of the phenolic nuclei. This is achieved by mixing the intermediate phenol-formaldehyde condensation product in a hydrocarbon solvent with a small amount of a suitable catalyst in an autoclave. The condensation product is heated above 100° C., and ethylene oxide, propylene oxide-1,2, or both ethylene oxide and propylene oxide, either as a mixture or by sequential addition of first the propylene oxide and then the ethylene oxide, or vice versa, are charged into the autoclave until the pressure is in the vicinity of 75–100 p.s.i.

The reaction mixture is gradually heated until an exothermic reaction begins. The external heating is then removed, and alkylene oxide is added at such a rate that the temperature is maintained between about 150–160° C. in a pressure range of 80 to 100 p.s.i. After all of the alkylene oxide has been added, the temperature is maintained for an additional 10 to 20 minutes to assure substantially complete reaction of the alkylene oxide. The resulting product is the alkylene oxide adduct of an alkyl phenol-formaldehyde condensation product, in which the weight ratio of the oxide to the condensation product is between about 1:2 and 15:1, respectively, preferably 1:2 to 9:1. The molecular weight of the oxyalkylated phenol-formaldehyde condensation products of this invention range from as low as about 1100 to as high as about 50,000. The weight ratio of oxyethylene to oxypropylene groups in the oxyethylated-oxypropylated phenol-formaldehyde resins will ordinarily be between about 4:1 and 1:25, respectively.

Some preferred embodiments of the oxyalkylated, alkyl phenol-formaldehyde condensation products and methods of their preparation are illustrated in the following examples wherein all parts are by weight unless otherwise stated, but the invention is not limited thereto.

Example F

In an autoclave having a two-liter capacity equipped with means of external electrical heating, internal cooling coils and mechanical agitation, there is charged 18 parts of the resin solution of Example B and 1.5 parts of sodium hydroxide. Into a transfer bomb there is introduced 23 parts of mixed oxides prepared by mixing equal parts of ethylene and propylene oxide by weight. The intermediate is heated to 135° C. and the oxide mixture is charged into the reactor until reactor pressure is 80 p.s.i. The reaction mixture is gradually heated until an exothermic reaction begins to take place. The external heating is removed and the mixed oxides are then added at such a rate that

the temperature is maintained between 150–160° C. with a pressure range of 80 to 100 p.s.i. At various stages in the reaction small samples of the reaction product were removed. After approximately 2 hours all of the oxide has been added to the autoclave and the temperature is maintained for an additional period of time so that the reactor pressure drops to a constant value. This may require from 15 minutes to 2 hours to make certain that the unreacted oxide is reduced to a minimum. The resultant product is the mixed oxide adduct of a phenol-formaldehyde resin in which the ratio of oxide to resin by weight is 4 to 1.

Example G

In a manner similar to Example F a mixed oxide adduct of the resin of Example A was prepared in which the ratio of ethylene oxide to propylene oxide was 1 part to 2 parts. The finished product is an oxyalkylated resin in which the ratio of mixed oxides to resin is 4 to 1.

Example H

In the same facilities as used in Example F, there is charged 172 parts of the resin solution of Example A and 1 part of sodium hydroxide. Into a transfer bomb there is introduced 250 parts by weight of ethylene oxide and 250 parts of propylene oxide. The intermediate is heated to 135° C. and the mixed oxides are charged into the reactor until the reactor pressure is 80 p.s.i. The reaction conditions from here on were identical with those employed in Example F. The resulting product is the mixed oxide adduct of a phenol formaldehyde resin in which the ratio of oxide to resin by weight is approximately 4 to 1.

Example J

In a manner similar to Example H. using a 1 to 3 by weight ratio of ethylene oxide to propylene oxide, a mixed oxide adduct of the resin of Example B was prepared in which the ratio of oxide to resin was 2 to 1.

Example K

In a manner similar to Example H. using a 1 to 3 by weight ratio of ethylene oxide to propylene oxide, a mixed oxide adduct of the resin of Example C was prepared in which the ratio of oxide to resin was 6 to 1.

Example L

In a manner similar to H, using a 1 to 3 by weight ratio of ethylene oxide to propylene oxide, a mixed oxide adduct of the resin of Example B was prepared in which the ratio of oxide to resin was 2 to 1.

Example M

In a manner similar to Example H. using a 3 to 1 by weight of ethylene oxide to propylene oxide, a mixed oxide adduct of the resin of Example A was prepared in which the ratio of oxide to resin was 1 to 1.

Example N

In a manner similar to Example H, there is prepared a propylene oxide adduct of the resin of Example A in which the ratio of propylene oxide to resin by weight is 1 to 1. The oxypropylated phenol-formaldehyde resin was then reacted further with ethylene oxide until the finished product contained 10% by weight of ethylene oxide.

Example O

In a manner similar to Example N, a propylene oxide adduct of the resin of Example C was prepared in which the ratio of propylene oxide to resin was 6 to 1 by weight. Ethylene oxide was then added to this oxypropylated phenol-formaldehyde resin until the finished product contained 20% by weight of ethylene oxide.

Example P

In a manner similar to Example N, a propylene oxide adduct of the resin of Example A was prepared in which the ratio of propylene oxide to resin was 9 to 1 by weight. This oxypropylated phenol-formaldehyde resin was then further reacted with ethylene oxide until the finished material contained 5% by weight of ethylene oxide.

Example Q

In a manner similar to Example N, a propylene oxide adduct of the resin of Example C was prepared in which the ratio of propylene oxide to resin was 2 to 1 by weight. This oxypropylated phenol-formaldehyde resin was then further reacted with ethylene oxide until the finished material contained 30% by weight of ethylene oxide.

Example R

Into the gas charge vessel of an oxyalkylation unit, is charged 250 parts of ethylene oxide and 250 parts of propylene oxide. The gases are circulated via a circulating pump to mix them thoroughly. Then 2000 parts of phenol-formaldehyde resin solution of Example D and 3.8 parts of sodium hydroxide are charged into the oxyalkylation. The reactor is purged with natural gas. The mixed oxides are added at 150–160° C. The oxyalkylation is completed at this temperature and a pressure of 80–100 p.s.i. The gases are recycled in the unit for two hours after the addition of oxides is complete. The resulting product is oxyalkylation product of the phenol-formaldehyde resin wherein the oxyethylene and oxypropylene groups are mixed heterogeneously in the oxyalkylene adduct radicals.

Example S

In a manner similar to Example R, 7200 parts of the resin solution of Example D and 1800 parts of an ethylene oxide-propylene oxide mixture (2 parts by weight propylene oxide per part ethylene oxide) are reacted in the presence of 13 parts of sodium hydroxide.

Example T

The mixed oxyethylene and oxypropylene adduct of the phenol-formaldehyde resin of Example E is prepared by substituting the resin solution of Example E for the resin solution of Example D in the procedure of Example S.

In using mixtures of the oxides in oxyalkylation, it is preferred that the weight ratio of ethylene oxide to propylene oxide be between 1:4 and 4:1. A considerably lower ratio of ethylene oxide to propylene oxide to about 1:25 may be employed where the oxides are added sequentially in the manner heretofore described—as evidenced by Example P.

Example FE

In an autoclave having a two-liter capacity equipped with a means of external electric heating, internal cooling coils and mechanical agitation, there is charged 400 parts of the condensation product of Example A and 2 parts of sodium hydroxide. Into a transfer bomb there is introduced 835 parts ethylene oxide. The condensation product is heated to 135° C., and the ethylene oxide is charged into the reactor until reactor pressure is 80 p.s.i. The reaction mixture is gradually heated until an exothermic reaction begins to take place. The extrenal heating is then removed and ethylene oxide is then added at such a rate that the temperature is maintained between 150°–160° C. with a pressure range of 80 to 100 p.s.i. After approximately six hours all of the oxide has been added to the autoclave, and the temperature is maintained for an additional 15 minutes to make certain that the unreacted oxide is reduced to a minimum. The resulting product is the ethylene oxide adduct of a phenol-formaldehyde condensate, in which the ratio of oxide to condensate by weight is 2 to 1.

Example GE

In a manner similar to Example FE, the ethylene oxide adduct of the condensation product of Example A was prepared in which the ratio of ethylene oxide to condensation product was 2 to 3 by weight.

Example HE

In a manner similar to Example FE, the ethylene oxide adduct of the condensation product of Example B was prepared in which the ratio of ethylene oxide to condensation product was 1½ to 1 by weight.

Example JE

In a manner similar to Example FE, the ethylene oxide adduct of the condensation product of Example B was prepared in which the ratio of ethylene oxide to condensation product was 2 to 1 by weight.

Example KE

In a manner similar to Example FE, the ethylene oxide adduct of the condensation product of Example C was prepared in which the ratio of ethylene oxide to condensation product was 1.5 to 1 by weight.

Example LE

In a manner similar to Example FE, the ethylene oxide adduct of the condensation product of Example C was prepared in which the ratio of ethylene oxide to condensation product was 2 to 1 by weight.

Example ME

In a manner similar to Example FE, the ethylene oxide adduct of the resin of Example D is prepared in which the weight ratio of ethylene oxide to condensation product is 1 to 1.

Example NE

In a manner similar to Example FE, the ethylene oxide adduct of the condensation product of Example E is prepared in which the weight ratio of ethylene oxide to condensation product is 1.5 to 1.

Example FP

In an autoclave having a nominal capacity of 5 gallons, equipped with a means of external heating, cooling and mechanical agitation, there is charged 17 pounds of the alkyl phenol-formaldehyde resin of Example A and one-tenth pound sodium hydroxide. Into a transfer bomb there is introduced 26 pounds of propylene oxide. The resin intermediate is heated to 135° C., and the propylene oxide is charged into the reactor until reactor pressure is 50 p.s.i. The reaction mixture is gradually heated until an exothermic reaction begins to take place. The external heating is then removed, and propylene oxide is added at such a rate that the temperature is maintained between 135–145° C., with a pressure range of 50–80 p.s.i. After approximately two hours all of the oxide has been added to the autoclave and the temperature is maintained for an additional period of time to allow the reactor pressure to fall to a constant level. This may require as long as an additional two hours of reaction time to make certain that the unreacted oxide is reduced to a minimum. The resulting product is the propylene oxide adduct of a phenol-formaldehyde resin in which the ratio of oxide to resin in which the ratio of oxide to resin by weight is 1½ to 1.

Example GP

In a manner similar to Example FP, the propylene oxide adduct of the resin of Example B was prepared in which the ratio of propylene oxide to resin was 1 to 1 by weight.

Example HP

In a manner similar to Example FP, the propylene oxide adduct of the resin of Example C was prepared in which the ratio of propylene oxide to resin was 2 to 1 by weight. The catalyst was potassium hydroxide.

Example JP

In a manner similar to Example FP, the propylene oxide adduct of the resin of Example C was prepared in which the ratio of propylene oxide to resin was 6 to 1 by weight.

Example KP

In a manner similar to Example FP, the propylene oxide adduct of the resin of Example A was prepared in which the ratio of propylene oxide to resin was 9 to 1 by weight.

Example LP

In a manner similar to Example FP, the propylene oxide adduct of the resin of Example A was prepared in which the ratio of propylene oxide to resin was 1 to 2 by weight.

Example MP

In a manner similar to Example FP, the propylene oxide adduct of the resin of Example C was prepared in which the ratio of propylene oxide to resin was 1 to 1 by weight.

Example NP

Using the procedure of Example FP the resin of Example D was reacted with 11.3 mols of propylene oxide and 3.3 mols of ethylene oxide. This provided a weight ratio oxides to resin of 2.4:1.

GLYCOL ESTERS

The second group of useful condensation products have the following structural formula:

$$R'(OC_nH_{2n})_xR$$

wherein R′ is either hydrogen, an alkyl, alkenyl, aralkyl, aralkenyl, cycloalkyl, aryl, or acyl radical; R is either hydroxy, oxyalkyl, oxyaralkyl, oxycycloalkyl, oxyaryl, secondary or tertiary aminoalkyl, secondary or tertiary aminoaryl, or oxyacyl; *n* is 3 or both 2 and 3 in a single molecule and *x* is equal to the number of times *n* is 3 or is the sum of the number of times *n* has a value of 2 plus the number of times that *n* has a value of 3 and the maximum ratio of *n* having a value of 2 to *n* having a value of 3 in such that the weight ratio of oxyethylene to oxypropylene does not exceed 4 to 1, it being further understood that the molecular weight of said composition is in excess of 1000 when both the oxyethylene and the oxypropylene groups are present in the same molecule and in excess of 1200, preferably at least 2000, when the oxyalkylene groups consist solely of oxypropylene groups.

All of the compounds employed for the purpose of this invention are characterized by the nucleus

$$—(OC_nH_{2n})_x—$$

wherein *n* has a value of 3, or both 2 and 3 in a weight ratio not exceeding 4 to 1, and a major proportion, preferably at least 60% by weight of the compound, is attributable to this nucleus. The total molecular weight is preferably in the range of 1500 to 7500.

As typical examples of compositions which are included in this invention, there can be mentioned heteric poly-oxyalkylene diols in which R′ is represented by the hydrogen atom and R by the hydroxyl group; monoethers of heteric polyoxyalkylene diols in which R′ is represented by an alkyl, alkenyl, aralkyl, aralkenyl, cycloalkyl, or aryl radical and R is represented by the hydroxyl group; diethers of heteric polyoxyalkylene diols in which R′ is represented by an alkyl, aralkyl, cycloalkyl or aryl radical and R by oxyalkyl, oxyaralkyl, oxycycloalkyl or oxyaryl radical; monoesters of heteric polyoxyalkylene diols in which R′ is represented by an acyl radical and R by the hydroxyl group; diesters of heteric polyoxyalkylene diols in which R′ is represented by an acyl radical and R by an oxyacyl radical; amine compositions in which R′ is represented by hydrogen and R by secondary or tertiary aminoalkyl, secondary or tertiary aminoaralkyl, secondary or tertiary aminoaralkyl, secondary or tertiary aminoaralkyl, secondary or tertiary amino-cycloalkyl, secondary or tertiary aminoaryl and chain substituted carboxy acids derived from hydroxy carboxy acids. It is to be understood that the substitution of hydrogen by halogen, nitro, hy-

droxyl, sulfonic and the like in the above radical does not depart from the scope of this invention for simple substitution products of this nature have been found to be equally satisfactory for the purposes as outlined herein.

It is not intended that the foregoing lists each and every heteric polyoxyalkylene oxide composition that will satisfactorily resolve water-in-oil emulsions in accordance with this invention, for it will be obvious to those skilled in the art that certain mixed derivatives of heteric polyoxyalkylene diols, one may mention the monoester-monoether, the monoester-monoamine, etc.

In order that these heteric polyalkylene oxide compositions possess the properties of efficiently breaking petroleum emulsions, they should be of relatively high molecular weight. Generally stated, it may be said that these compositions employed for the purposes of this invention may be characterized as having a total average molecular weight of at least 1000 and the hetero polyoxyalkylene groups constitute a major proportion of this molecular weight.

These demulsifying compounds employed for the purposes of the invention may be also described as being surface active and water wettable, and those which do not possess a nitrogen atom, a sulfonic group, and/or a carboxyl group within the molecule may be described as being nonionic in that they do not ionize to yield organic cations or organic anions.

The compounds employed in accordance with this invention may be prepared in several ways. For example, U.S. Patent 2,425,845 describes the method of preparing heretofore polyoxyalkylene diols. Briefly, good results may be obtained by placing a mixture containing the ethylene oxide and the propylene oxide into intimate contact with a dihydroxy aliphatic alcohol, in a liquid phase throughout which a suitable catalyst is uniformly dispersed. For best results, it is essential that the addition reaction be carried out under conditions which are controlled with respect to such factors as the amount of active catalyst employed and the uniformity of its dispersion, the amount of unreacted alkylene oxides present at all stages during the reaction, the temperature maintained throughout the course of the reaction and particularly the intimacy and uniformity of contact of the reactants during the process. As a catalyst, sodium hydroxide or potassium hydroxide is preferred in amount which is about 0.2 to 1% by weight of the reactants. Excessive concentrations of unreacted alkylene oxides are to be avoided and pressures of 5 to 50 pounds per square inch are preferred for reaction conditions.

Compositions suitable for the practice of the invention can also be prepared by adding the alkylene oxides successively, rather than concurrently, to an initial starting material containing a reactive hydrogen atom, as, for example, a monohydric alcohol, a polyhydric alcohol or a primary or secondary amine. Thus, 1,2-propylene oxide can be added to such a starting material followed by ethylene oxide. Similarly, ethylene oxide can be added directly to a long chain preformed polyoxypropylene glycol to produce compositions suitable for the practice of the invention. For example, 1,2-propylene oxide can be polymerized to produce a long chain polyoxypropylene glycol containing 35 mols of 1,2-propylene oxide and 4 to 12 mols of ethylene oxide are added to produce a polyoxyethylated polyoxypropylene diol. This composition can be used as such in the practice of the invention or employed as an intermediate in making ethers, esters and amine addition products in the manner herein described which are also suitable for the practice of the invention. All of these compositions are characterized by the fact that they contain at least one long oxyalkylene chain composed of oxypropylene groups or both oxyethylene and oxypropylene groups in which the molecular weight attributable to such oxyalkylene groups is at least 1200 when the oxyalkylene groups are all oxypropylene groups and at least 1000 when the oxyalkylene groups are both oxyethylene and oxypropylene groups with the further proviso in the latter case that the weight ratio of oxyethylene to oxypropylene cannot exceed 4:1. The presence of too many oxyethylene groups detracts from the effectiveness of the composition in breaking water-in-oil emulsions.

The preparation of monoethers of hetero polyoxyalkylene diols has been described in U.S. Patent 2,425,755. Briefly, these products are prepared by placing the ethylene oxide and propylene oxide mixture into intimate contact with the monohydroxy alcohol in a liquid phase throughout which a suitable catalyst is uniformly dispersed. As a catalyst, sodium hydroxide or potassium hydroxide is preferred in an amount which is about 0.2% to 1% by weight of the total amount of reactants. All of the catalyst need not be added at the start of the reaction. The reaction can be successfully carried out at temperatures of 80° C. to 160° C. which is sufficiently high to favor rapid reaction of the alkylene oxides. Pressures comparable for the manufacture of the diols have been found to be satisfactory for production of the monoethers. Excessive concentrations of unreacted alkylene oxide are also avoided. In order to discourage the formation of undesired side reaction products, the vessel is preferably swept out with gaseous nitrogen to remove oxygen which is conductive to undesired side reactions.

The above reaction may be represented by the following equation where the mixture of ethylene oxide and propylene oxide is used.

$$ROH+y(CH_2CH_2O)+z(CH_3H_2H_3O)\rightarrow R(OC_nH_{2n})_xOH$$

In the foregoing equation, ROH is an aliphatic monohydrxy alcohol; y and z represent the mols of ethylene oxide and 1,2-propylene oxide respectively; n is both 2 and 3 is a single molecule, the total number of times n has a value of 3 being equal to z; and x is the total number of such oxyalkylene groups, being equal to y plus z. Methods of effecting this reaction with the mixed oxides and the resultant compositions have been described in U.S. Patent 2,425,755. Certain modifications of this general reaction may be employed to produce compositions of the practice of the present invention, e.g., in place of the aliphatic monohydroxy alcohol (ROH), the alkylene or mixed oxides may be reacted with a polyoxyalkylene monohydroxy alcohol prepared by this or some other route, to result in a product of the same chemical nature but of increased molecular weight because of the increased length of the polyoxyalkylene chain.

Another way in which the same class of products may be prepared is to effect the reaction of an alkyl, aryl, cycloalkyl, or aralkyl halide with an alkali metal alcoholate. Much work on this general preparative scheme has been done by Hibbert and his coworkers (see e.g., Journal American Chemical Society, vol. 61, p. 1905). The two equations given below illustrate the reaction involved.

$$RX+Na(OC_2H_4)_xOH\rightarrow R(OC_2H_4)_xOH+NaX$$

$$RX+Na(OC_3H_6)_xOH\rightarrow R(OC_3H_6)_xOH+NaX$$

In these equations, R represents alkyl, aralkyl, aryl or cycloalkyl, x is a whole number, and X is halogen, e.g., chlorine or bromine. For convenience, polyoxyethylene glycols and polyoxypropylene glycols have been used for illustration but it will be understood that polyoxyalkylene gycols containing both oxyethylene and oxypropylene groups in the same molecule will undergo the same type of reaction.

The symmetrical diethers of the hetero polyoxyalkylene diols may be prepared by reaction of two molecular proportions of the desired alkyl, aryl, aralkyl or cycloalkyl halide with one molecular proportion of the di-

sodium salt of the hetero polyoxyalkylene diol according to the following equation:

$$2RX+Na(OC_nH_{2n})_xONa \rightarrow R(OC_nH_{2n})_xOR+2NaX$$

where R is alkyl, aryl, aralkyl or cycloalkyl, X is halogen, n is both 2 and 3 and x is some whole number.

By starting with the dihalide derivative of the hetero polyoxyalkylene diol and reacting one molecular proportion thereof with two molecular proportions of a sodium alcoholate, the same type of products will result.

One may start with the monoether of a hetero polyoxyalkylene diol prepared in accordance with the procedure outlined above and react it with sodium to give the corresponding alcoholate. This alcoholate may then be reacted in accordance with Equation 1 below with any desired alkyl halide to yield diethers of the hetero polyoxyalkylene diol or in accordance with Equation 2 with an alkylene dihalide to give a diether of a hetero polyoxyalkylene diol. These reactions are illustrated in the following two equations:

(1) $$R(OC_nH_{2n})_xOH + Na \longrightarrow R(OC_nH_{2n})_xONa \xrightarrow{RX} R(OC_nH_{2n})_xOR + NaX$$

where R is alkyl, X is halogen, n is both 2 and 3 and x is a whole number such that the molecular weight is at least 1000.

(2) $$2R(OC_nH_{2n})_xONa+X(C_nH_{2n})X \rightarrow [R(OC_nH_{2n})_xO]_2C_nH_{2n}+2NaX$$

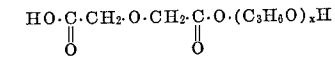
where R, n, and X have the same significance as in the previous equation.

Although the above procedures have been discussed under the heading of the preparation of symmetrical diethers, it is to be understood that by proper choice of the reaction procedure unsymmetrical diethers can be prepared which are suitable for the purpose of this invention. The preferred compositions employed for the practice of this invention are esters of an organic carboxy acid and an organic non-acidic hydroxy compound having a hydroxyl group attached to an acyclic carbon atom and esterified with said carboxy acid and further characterized by having oxyalkylene groups from the class consisting of oxypropylene and both oxyethylene and oxypropylene in a weight ratio of oxyethylene to oxypropylene not exceeding 4:1 in the same molecule form the major proportion of the average molecular weight of said ester being predominantly monomeric exclusive of said oxyalkylene groups and containing a long uninterrupted oxyalkylene chain composed of said oxyalkylene groups in which the molecular weight attributable to said oxyalkylene groups in said long chain is at least 1000 when the oxyalkylene groups are both oxyethylene and oxypropylene and at least 1200 where the oxyalkylene groups are solely oxypropylene groups.

The monoesters and diesters of hetero polyoxyalkylene diols are prepared in accordance with recognized and established procedures for such synthesis. The most simple manner of preparing the monoesters or diesters is by reacting the diol with the required acid anhydride. In many instances the reaction will proceed without the application of external heat. For the purposes of this invention, the presence of a small quantity of residual free acid is not harmful to the resulting demulsifying characteristics of the ester compounds. In those instances where acid anhydrides are not readily available, or if it is desired that the resulting product contain no free acid, the diol may be reacted with the required acid in the presence of a solvent which lends itself to azeotropic distillation. The reaction mass is then heated at elevated temperatures until the theoretical amount of water has been secured to indicate substantial esterification. Both symmetrical and unsymmetrical diesters can be prepared with these procedures and the resulting compositions are effective in demulsifying water-in-oil emulsions. Further, it has been noted that both mono- and diesters of polybasic acids, when one or more of the carboxyl groups remain unreacted, are particularly effective as demulsifiers. It has been found that both organic acids, as well as inorganic acids, such as boric, phosphoric, arsenic and the like, are suitable esterifying acids for purposes of this invention.

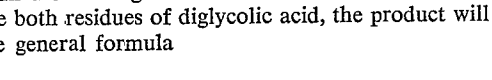
The reaction conditions employed in the preparation of esters for the purpose of the invention are esterifying conditions which will vary somewhat depending upon the reactants but normally involve the reaction of an esterifying acid with a compound having a hydroxyl group connected to an acyclic carbon atom at temperatures within the range of 50° C. to 300° C. for a period of time from 2 to 12 hours. If the starting materials contain more than one hydroxyl group and/or more than one acid group, the resultant compositions are cogeneric mixtures of esters but under these reacting conditions, in view of the fact that the hydroxy-containing compound must also contain at least one long oxyalkylene chain having a molecular weight of at least 1000 as herein described, the mixtures are predominantly monomeric esters. In other words, the predominating components of the mixtures are esters which contain a single ester linkage connecting the residue of the acid with a long oxyalkylene chain of the type described or a single long oxyalkylene chain connected at opposite ends to ester linkages or another type of chemical structure wherein the ester groups and the long oxyalkylene chains do not recur in the same molecule. Especially good results in the practice of the invention have been obtained by the use of predominantly monomeric dicarboxy acid esters of aliphatic hydroxy compounds having a terminal hydroxyl group connected to a long polyoxyalkylene chain in which the oxyalkylene groups are composed of oxypropylene groups or both oxyethylene groups and oxypropylene groups with a weight ratio of oxyethylene to oxypropylene not exceeding 4:1 and the average molecular weight attributable to said oxyalkylene groups in said chain is at least 1200 where the oxyalkylene groups are solely oxyproplene groups and at least 1000 where the oxyalkylene groups are both oxyethylene and oxypropylene groups. The preferred dicarboxy acids for the purpose of preparing the foregoing esters are those containing to 8 carbon atoms and especially maleic anhydride, diglycolic acid and phthalic anhydride.

In the general formula $R'(OC_nH_{2n})_xR$ when n is 3, R' is hydrogen and R is the residue of diglycolic acid, the product will have the formula



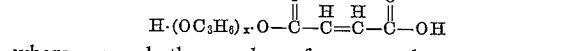
where x equals the number of oxypropylene groups present in a polyoxypropylene glycol having a molecular weight of at least 1200. As will be apparent from the foregoing description this product is obtained by reacting one mol of diglycolic acid with one mol of a polyoxypropylene glycol having a molecular weight of at least 1200.

In the same general formula if n is 3 and R' and R are both residues of diglycolic acid, the product will have the general formula

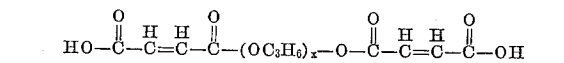


where x equals the number of oxypropylene groups present in a polyoxypropylene glycol having a molecular weight of at least 1200. This product is obtained by reacting two mols of diglycolic acid with one mol of a polyoxypropylene glycol having a molecular weight of at least 1200.

If maleic anhydride is used instead of the diglycolic acid, the formulae of the respective products are

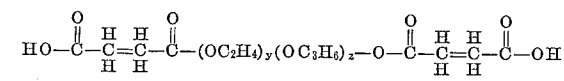


where x equals the number of oxypropylene groups present oxypropylene glycol having a molecular weight of at least 1200, and



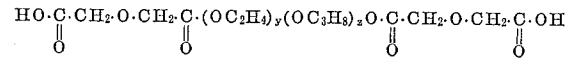
where x equals the number of oxypropylene groups present in a polyoxypropylene glycol having a modecular weight of at least 1200.

If in the general formula $R'(OC_nH_{2n})_xR$ n is both 2 and 3, the product where two mols of maleic anhydride are reacted with one mol of a high molecular weight polyoxyalkylene glycol has the general formula



where y and z represent the number of oxyethylene and oxypropylene groups, respectively.

If diglycolic acid is used instead of the maleic anhydride, the product has the formula



where y and z represent the number of oxyethylene and oxypropylene groups, respectively.

The secondary amino and tertiary amino derivatives having hetero polyoxyalkylene groupings are prepared by intimately mixing for example, ethylene oxide, propylene oxide and either a primary or secondary amine, respectively, in a reaction vessel. An alkaline catalyst, such as sodium hydroxide or potassium hydroxide, is to be preferred and should be uniformly dispersed throughout the reaction mixture. Conditions similar to those previously described in the preparation of polyoxyalkylene diols and monoethers of hetero polyoxyalkylene diols should be maintained for optimum results.

A substituted chain carboxy acid composition having hetero polyoxyalkylene groups is prepared under similar conditions by using, for example, the methyl ester of glycolic acid, where the glycolate, ethylene oxide and propylene oxide are intimately mixed and a catalyst is chosen such that it is not sufficiently alkaline to saponify the starting ester. Optimum conditions are similar to those outlined for the preparation of diols and monoethers.

A still further type of composition having hetero polyoxyalkylene groupings that has been found to be an effective demulsifier can be prepared by reacting a polyoxyethylene glycol and a polyoxypropylene glycol with formaldehyde in the presence of an acid catalyst. The resulting compositions are broadly classed as polyformal derivatives. By varying the types of glycols and the relative quantities of the glycols used as starting materials one can secure compounds having hydrophobe-hydrophile balances which extend from one extreme to the opposite extreme.

Since, as indicated above, it is possible to prepare the compositions of this invention by various routes, and from a number of different classes of starting materials, the invention should not be limited by the following examples, which are merely intended to illustrate some satisfactory procedures for preparing a few of the materials suitable for employment within the scope of the present invention.

Example I

Step I.—A polyoxyalkylene glycol starting material of relatively low molecular weight was made by introducing a mixture of 18 parts of ethylene oxide and 6 parts of 1,2-propylene oxide into a suitable reactor charged with 20 parts of diethylene glycol and 1.56 parts of dry powdered sodium hydroxide intimately dispersed therein. The reaction mixture was vigorously agitated and maintained at a temperature of about 119° C. to 127° C. throughout the reaction. About 18 minutes were required to feed in the oxides which were supplied at a rate to maintain a pressure of 16 p.s.i. After all of the oxides had been charged the reaction mixture was recycled for a period of 30 minutes.

Step II.—A mixture of 60 parts of ethylene oxide and 20 parts of 1,2-propylene oxide was introduced into a reactor containing 20 parts of the product of Step I at a rate to maintain a pressure of about 22 to 30 p.s.i. over a period of about 1 hour. No adidtional sodium hydroxide was added and a temperature of about 111° C. to 122° C. was maintained during the reaction and the reaction mixture recycled for about ½ hour after all of the oxides had been introduced. The product was a liquid and was neutralized with dilute sulfuric acid and filtered to yield a diol composition having a molecular weight of about 1,060.

Example II

Step I.—Ninety-five (95) parts by weight of a mixture of equal amounts of ethylene oxide and propylene oxide were introduced into 20 parts of butyl alcohol containing 1 part of powdered sodium hydroxide dispersed therein. The temperature was raised to about 115° C. and the oxide mixture was introduced into the butyl alcohol at such a rate that the pressure was maintained at about 26 p.s.i. over a period of about 3 hours.

Step II.—To 40 parts by weight of the reaction product of Step I was added 0.5 part by weight of powdered sodium hydroxide followed by 70 parts by weight of a mixture of equal parts of ethylene oxide and propylene oxide. The temperature was maintained at 113° C. during the reaction, and the oxide mixture supplied at such a rate as to maintain a pressure of about 22 p.s.i. The reaction time was about 2 hours. The reaction product of this step was neutralized with dilute sulfuric acid and filtered to yield the monoether polyoxyalkylene diol compound.

Example III

A solution of sodium isopropoxide was prepared from sodium and substantially anhydrous isopropanol. To 205 parts of sodium isopropoxide was added 340 parts of the monobutyl ether of a polyoxyalkylene glycol, the polyoxyalkylene chain of which contained ethylene oxide and propylene oxide in a 1:1 ratio, and the total molecular weight (for the butyl ether) of which was approximately 1700. The reaction was refluxed for one hour and the isopropanol was removed under reduced pressure until the theoretical amount had been secured. The resulting sodium salt of the monoether diol was cooled and 13.7 parts of butyl bromide was added drop-wise with stirring over a period of about 30 minutes. The reaction mass was allowed to continue with stirring to 110° C. until a test for alkalinity to phenolphthalein was negative, which required about 1 hour. The reaction mixture was then diluted with isopropanol to facilitate the subsequent filtration in order to remove the precipitated sodium chloride. The isopropanol was then removed by heating to 100° C. under reduced pressure to yield the diether of of a heteric polyoxyalkylene diol.

Example IV

To 1,060 parts of diol as prepared in Example I contained in a suitable reaction flask there was added 300 parts of oleic acid and 100 parts of a hydrocarbon diluent such as SO_2 extract. The reaction mixture was heated to 160° C. to 220° C. until an amount of water had distilled over equivalent to the theoretical amount required for esterification. If it is desired that the monoester be isolated in substantially pure form, the hydrocarbon vehicle may

be removed by heating at elevated temperatures under vacuum.

The diester may be prepared in a similar manner by using 600 parts of oleic acid instead of the 300 parts required for the preparation of the monoester.

Example V

In a suitable reaction flask there was placed 500 parts of a monoether of a heteric polyoxyalkylene diol having a molecular weight of 5000 as prepared similar to the directions of Example II, 15 parts of maleic anhydride and 100 parts of SO_2 extract. At approximately 50° C., the maleic anhydride melted and apparently added to the terminal—OH by opening of the anhydride linkage. To insure complete reaction, the reaction mixture was heated for 4 hours at 200° C. This yield the monoether-monoester composition having a residual free carboxyl group.

Example VI

Step I.—Ninety-five (95) parts by of the mixture of equal amounts of ethylene oxide and propylene oxide were introduced into 20 parts by weight of n-butanol containing 1 part of powdered sodium hydroxide dispersed therein. The temperature was maintained at about 105° C. and the oxide mixture was introduced into the butylamine at such a rate that the pressure was maintained at about 20 p.s.i. over a period of about 3 hours.

Step II.—To 30 parts by weight of the reaction product of Step I was added 0.5 part by weight of powdered sodium hydroxide, followed by 70 parts by weight of a mixture of equal parts of ethylene oxide and 1,2-propylene oxide. The temperature was maintained at 105° C. during the reaction and the oxide mixture supplied at such a rate as to maintain a pressure of about 18 p.s.i. The reaction product of this step was a heteric polyoxyalkylene amine composition having a molecular weight of approximately 1000.

Example VII

Step I.—Ninety-five (95) parts by weight of a mixture of equal amounts of ethylene oxide and propylene oxide were introduced into 22 parts by weight of methyl glycolate containing 1 part of boron trifluoride dispersed therein. The temperature was maintained at about 115° C. and the oxide mixture was introduced into the methyl glycolate at such a rate that the pressure was maintained at about 26 p.s.i. over a period of about 3 hours.

Step II.—To 40 parts by weight of the reaction product of Step I was added 0.5 part by weight of boron trifluoride, followed by 70 parts by weight of a mixture of equal parts of ethylene oxide and 1,2-propylene oxide. The temperature was maintained at about 115° C. during the reaction, and the oxide mixture supplied at such a rate as to maintain a pressure of about 22 p.s.i. The reaction time was about 2 hours. The reaction product was a chain substituted carboxy acid ester wherein the chain is composed of heteric polyoxyalkylene groupings.

Example VIII

In a suitable reaction flask 60 parts of a polyoxyethylene glycol having a molecular weight of 400, 152 parts of a polyoxypropylene glycol having a molecular weight of 2000, 7 parts of trioxymethylene, 1 part ferric chloride and 150 parts of benzene were heated. During the course of the reaction 4.6 parts of water were azeotropically distilled from the reaction mass and discarded. The resulting polyformal derivative may be used as such or can be isolated by filtering and removing the benzene under reduced pressure.

Example IX

To 220 parts of a hetero polyoxyalkylene diol having a molecular weight of 2200 (wherein the oxypropylene groups constitute 25% by weight and the oxyethylene groups 75% by weight of the oxyalkylene groups present) contained in a suitable reaction flask there is added 30 parts of phthalic anhydride and 100 parts of a hydrocarbon diluent such as SO_2 extract. The reaction mixture is heated to 155° C. and held at that temperature for a period of 5 hours. Esterification is accomplished by the opening of the anhydride linkage to completely esterify both hydroxy groups of the starting diol. After cooling to approximately 100° C., 400 parts of a hydrocarbon diluent such as SO_2 extract is added to yield the finished product.

Example X

To 400 parts of a polyoxypropylene glycol having a molecular weight of 2000 contained in a suitable reaction flask there is added 75 parts of phthalic anhydride. The reactants are heated with agitation for a period of 12 hours at a temperature of 230° C. Somewhat elevated temperatures are required to secure esterification by opening of the anhydride linkage on account of the fact that at least a portion of the hydroxy groups present in the diol are secondary and not as reactive as primary hydroxy groups. In order to secure the finished product, 900 parts of a suitable hydrocarbon extract is added and agitated to secure uniform solution of the ester.

Example XI

To 850 parts of a monobutyl ether of a hetero polyoxyalkylene diol having a molecular weight of 1700 contained in a suitable reaction flask there is added 15.5 parts of substantially anhydrous boric acid and 200 parts of a hydrocarbon diluent such as SO_2 extract. The reaction mixture is heated to 170° C. to 208° C. for 3 hours or until such time as an amount of water has distilled equivalent to the theoretical amount required for esterification. The resulting product will have one acidic replaceable hydrogen which has not been reacted with an alcoholic hydroxyl group. The product as above prepared may be used as a surface active material, as well as an emulsion breaking reagent.

Example XII

To 300 parts of polyoxypropylene glycol having a molecular weight of 2000 contained in a suitable reaction flask there is added 3.6 parts of phosphorous pentoxide. The reaction mixture is heated with stirring for 8 hours at 185° C. to 195° C. The resulting product is a phosphoric acid ester of a polyoxypropylene glycol and may be dissolved in suitable solvents for ease of subsequent handling.

Example XIII

In a suitable reaction flask there is placed 1000 parts of polyoxypropylene glycol having a molecular weight of 2000, 74 parts of phthalic anhydride and 2000 parts of a suitable hydrocarbon fraction such as SO_2 extract. The phthalic anhydride reacts at approximately 150° C. by opening of the anhydride linkage to form the monophthalate of the polyoxypropylene glycol.

Example XIV

The butyl ether of polyoxypropylene glycol having a molecular weight of 1200 is prepared by the reaction of butyl bromide with the alkali metal alcoholate of the polyoxypropylene glycol.

To 653 parts of the monobutyl ether of a polyoxypropylene glycol, prepared as above, contained in a suitable reaction flask, there is added 150 parts of talloil (which is essentially an equal mixture of unsaturated acids and resin acids) and 300 parts of SO_2 extract. The reaction mixture is heated until an amount of aqueous distillate has been secured which is equivalent to the theoretical amount of water required for complete esterification. This requires a reaction time of approximately 4 hours and temperatures between 170° C. and 220° C. The finished product is the talloil ester of the butyl ether of the polyoxypropylene glycol.

Example XV

A heteric polyoxyalkylene diol having a molecular weight of approximately 1500 is prepared in accordance with the procedure described in U.S. Patent 2,425,845.

To 750 parts of the diol as prepared above there is added 150 parts of oleic acid and 100 parts of a hydrocarbon diluent such as SO_2 extract. The reaction mixture is heated at 160° C. to 220° C. until an amount of water has distilled over equivalent to the amount required for esterification. The reaction material is the monooleic ester of the heteric diol.

Example XVI

In a suitable reaction flask there is placed 500 parts of a monobutyl ether of a heteric polyoxyalkylene diol having a molecular weight of 5000, as prepared in accordance with the procedure described in U.S. Patent 2,425,755, 15 parts of maleic anhydride and 100 parts of SO_2 extract. At approximately 150° C. the maleic anhydride dissolves and forms the monoester by adding to the terminal hydroxyl group by opening of the anhydride linkage. To insure complete reaction the reaction mixture is heated for 4 hours at 200° C. This yields the monoether-monoester composition having a free residual carboxyl group.

Example XVII

In a suitable reaction flask there is placed 850 parts of a butyl ether of a heteric polyoxyalkylene diol having a molecular weight of approximately 1700 as prepared similarly to the directions of Example XIV, 34 parts of diglycolic acid and 100 parts of SO_2 extract. The reaction mixture is heated and an aqueous distillate begins to form at 208° C. After 5 hours heating and a maximum temperature of 257° C., a total of 9 parts of aqueous distillate is secured to yield the didiglycolic ester of the monobutyl heteric diol ether.

Example XVIII

In a suitable reaction flask were placed 660 parts of a polypropylene glycol having a molecular weight of 4000. To this charge was added 8 parts of diglycolic acid and 1 part of water and a small amount of SO_2 extract. The flask was heated to 265° for 3½ hours. At the end of this time the final esterification was complete. This produced a polyester.

As indicated, preferred compositions which are combined with the aliphatic polycarboxylic acids are a blend of the phenolformaldehyde condensation products with the glycol esters, said materials being combined to provide a weight ratio within the range of 1:6 to 6:1.

It will be understood that the major concept of the invention resides in using the aliphatic polycarboxylic acids, per se.

EVALUATION OF THE INVENTION

To determine the effectiveness of the additives as emulsion preventatives and breakers, the following experimental procedure was used:

One hundred ml. stoppered graduates are filled with treated gasoline [1] to the eighty ml. graduation. The emulsion breaker is then added, using a 1% solution so that low concentrations can be tested. The sample is thoroughly agitated to mix in the emulsion breaker. Twenty mls. of distilled water are added and the sample is again shaken for one minute. Water clarity and gasoline brightness are noted after five minutes. A specially treated gasoline prepared by a communal refinery is used as a standard of performance.

Gasoline dilution.—The effect of the emulsion breaker on various levels of the deicer was studied in base gasoline diluted samples of the treated gasoline.

[1] Contains 100 p.p.m. each of a commercial amine salt, corrosion inhibitor and carburetor antiicing additives.

Using the above procedure a number of carboxylic acids were tested. The results of these tests are presented below in Table I. From Table I it is evident that only diglycolic, citric, fumaric and adipic acids were the only acids effectual in preventing the emulsion. This is striking when it is considered that maleic is ineffective even through it is an isomer of fumaric. The dosages in Table I are all 10 parts per million.

TABLE I.—ACIDS IN ORDER OF ACTIVITY

Acid	No. of carbon atoms	No. of carboxyl groups	Result
Diglycolic	4	2	Excellent.
Citric	6	3	Very good.
Fumaric	4	2	Good.
Adipic	6	2	Do
Azelaic	9	2	Fair.
Cinnamic	9	1	Poor.
Salicylic	7	1	Do.
Phthalic	8	2	Do.
Isophthalic	8	2	Do.
Terephthalic	8	2	Do.
Succinic	4	2	Do.
Acrylic	3	1	Do.
Lactic	3	1	Do.
Maleic	4	2	Do.
Glycolic	2	1	Do.
n-Valeric	5	1	Do.
Acetic	2	1	Do.
Cloroacetic	2	1	Do.
Benzylmalenic	10	2	Do.
Lauric	12	1	Do.

Although not shown in Table I, when the dosage of the four acids, e.g., diglycolic, citric, fumaric and adipic, exceeded 15 p.p.m., they promoted emulsion stability.

Using the same technique in the test method as set forth in Example I, additional tests were run blending diglycolic acid with various non-ionic wetting agents, the particular ratio used in all the tests was 1 part of the non-ionic wetting agent to 10 parts of the diglycolic. The particular group of non-ionic wetting agents that were most successful are set forth below.

Example XIX

The reaction product (esterification) of diglycolic acid (0.02 wt. percent), dimer acid (4.9 wt. percent), a 12.5 mole ethoxylated nonyl phenol-formaldehyde-diethylenetriamine resin (11.9 wt. percent) and a 8.6 mole ethoxylated nonyl phenol-formaldehyde resin (11.9 wt. percent) blended with a 6.2 mole ethoxylated nonyl phenol-formaldehyde resin (3.6 wt. percent) and an aromatic solvent (balance).

Example XX

The reaction product (esterified) of dimer acid (4.8 wt. percent) and a sequentially 4.5 mole propoxylated, 11.7 mole ethoxylated 3.0 mole fatty acid esterified tripentaerythritol (35.4%) blended with a 6.2 mole ethoxylated phenol-formaldehyde resin (2.3 wt. percent) and an aromatic solvent.

Example XXI

The reaction product of dimer acid (1.2 wt. percent), a 40.4 mole ethoxylated 44.8 mole polypropylene glycol (6.04 wt. percent), 8.6 ethoxylated nonyl phenol-formaldehyde resin (13.1 wt. percent), and a 2.0 plus mole diglycolic acid per mole 5.6 mole ethoxylated 44.8 mole polypropylene glycol reaction product (2.6 wt. percent) blended with a 6.2 mole ethoxylated nonyl phenol-formaldehyde resin (7.6 wt. percent) and an aromatic solvent.

Example XXII

A sequentially 3.5 mole propoxylated, 15.5 mole ethoxylated, 3.0 mole fatty acid esterified tripentaerythritol (96 wt. percent).

Example XXIII

8.6 mole ethoxylated nonyl phenol-formaldehyde resin (86.5 wt. percent).

Example XXIV

3.2 mole ethoxylated nonyl phenol-formaldehyde resin (79 wt. percent).

The most effective additive was diglycolic acid combined with a blend of the products of Example NP and XVIII combined in a weight ratio of approximately 1:1.

The acids used in the practices of the invention are for the most part insoluble in gasoline at the higher dosage levels recommended by the invention. To more conveniently use the materials commercially it is expedient to first dissolve the acids in a gasoline soluble polar organic solvent. Examples of such solvents are the lower aliphatic alcohols such as methanol, ethanol, propanol, isopropanol, butanol and t-butanol. Also useful solvents are the lower aliphatic glycol ethers such as the mono and dimethyl ethers of ethylene glycol.

When the acids are combined with the surface active agents the solvent formulas are conveniently prepared for use at the refinery level. An example of such a formula is presented below:

FORMULA

Component:	Percent by weight
Diglycolic acid	1
Product Example NP	.125
Product Example XVIII	.125
Aromatic petroleum solvent	10
t-Butanol	88.9

CONCLUSION

Based on the above it is evident that the invention provides a gasoline which has been inhibited against the tendency to form emulsions with water by adding to such gasolines less than 15 p.p.m. of certain chemical compositions. Due to the low dosage of the materials there is no tendency that the fuel characteristics of the gasoline are changed.

We claim:

1. A motor fuel for internal combustion engines comprising a major portion of gasoline which contains not more than 2% by weight of polar organic compounds from the group consisting of amines, amine salts and fatty imadazoline salts capable of preventing the corrosive and carburetor icing tendencies of said gasoline and from 0.1 to 15 p.p.m. of an aliphatic polycarboxylic acid from the group consisting of diglycolic acid, citric acid, fumaric acid and adipic acid.

2. The motor fuel of claim 1 where the aliphatic polycarboxylic acid is diglycolic acid.

3. The motor fuel of claim 1 where the aliphatic polycarboxylic acid is citric acid.

4. A motor fuel for internal combustion engines comprising a major portion of gasoline which contains not more than 2% by weight of polar organic compounds capable of preventing the corrosive and carburetor icing tendencies of said gasoline and from 0.1 to 15 parts per million of a composition comprising:

(A) An aliphatic polycarboxylic acid from the group consisting of diglycolic acid, citric acid, fumaric acid and adipic acid, and

(B) a non-ionic surface active agent with the weight ratio of A to B being within the range of from 1:1 to 10:3.

5. The motor fuel of claim 4 where the aliphatic polycarboxylic acid is diglycolic acid.

6. The motor fuel of claim 4 where the non-ionic surface active agent is an oxyalkylated alkyl phenol-formaldehyde condensation product having 4–15 phenolic nuclei, the alkyl group of said phenol having between 4 and 15 carbons, inclusive, the weight ratio of alkylene oxide to condensation product falling between about 2.5:1 to 1:2.5, respectively, the oxyalkylene groups of said oxyalkylated condensation product being selected from the group consisting of oxyethylene, oxypropylene and both oxyethylene and oxypropylene.

7. The motor fuel of claim 4 where the non-ionic surface active agent has the structural formula:

$$R'(OC_nH_{2n})_xR$$

wherein R' is either hydrogen, an alkyl, alkenyl, aralkyl, aralkenyl, cycloalkyl, aryl, or acyl radical; R is either hydroxyl, oxyalkyl, oxyaralkyl, oxycycloalkyl, oxyaryl, secondary or tertiary aminoalkyl, secondary or tertiary aminoaryl, or oxyacyl; n is 3 or both 2 and 3 in a single molecule and x is equal to the number of times n is 3 or is the sum of the number of times n has a value of 2 plus the number of times that n has a value of 3 and the maximum ratio of n having a value of 2 to n having a value of 3 is such that the weight ratio of oxyethylene to oxypropylene does not exceed 4 to 1, it being further understood that the molecular weight of said composition is in excess of 1000 when both the oxyethylene and the oxypropylene groups are present in the same molecule and in excess of 1200, preferably at least 2000, when the oxyalkylene groups consist solely of oxypropylene groups.

8. The motor fuel of claim 4 where the non-ionic surface active agent is a blend of

(1) an oxyalkylated alkyl phenol-formaldehyde condensation product having 4–15 phenolic nuclei, the alkyl group of said phenol having between 4 and 15 carbons, inclusive, the weight ratio of alkylene oxide to condensation product falling between about 2.5:1 to 1:2.5 respectively, the oxyalkylene groups of said oxyalkylated condensation product being selected from the group consisting of oxyethylene, oxypropylene and both oxyethylene and oxypropylene, and

(2) $$R'(OC_nH_{2n})_xR$$

wherein R' is either hydrogen, an alkyl, alkenyl, aralkyl, aralkenyl, cycloalkyl, aryl, or acyl radical; R is either hydroxy, oxyalkyl, oxyaralkyl, oxycycloalkyl, oxyaryl, secondary or tertiary aminoalkyl, secondary or tertiary aminoaralkyl, secondary or tertiary aminoaryl, or oxyacyl; n is 3 or both 2 and 3 in a single molecule and x is equal to the number of times n is 3 or is the sum of the number of times n has a value of 2 plus the number of times that n has a value of 3 and the maximum ratio of n having a value of 2 to n having a value of 3 is such that the weight ratio of oxyethylene to oxypropylene does not exceed 4 to 1, it being further understood that the molecular weight of said composition is in excess of 1000 when both the oxyethylene and the oxypropylene groups are present in the same molecule and in excess of 1200, preferably at least 2000, when the oxyalkylene groups consist solely of oxypropylene groups,

with the weight ratio of (1) to (2) being within the range of 1:6 to 6:1.

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44—63, 70, 71, 72; 252—340

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,424,565 January 28, 1969

Edward A. Ptacek et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 10, line 34, "hydrxy" should read -- hydroxy --; line 32, "ROH+y(CH_2CH_2O)+z($CH_3H_2H_3O$)-R(OC_nH_{2n})$_x$OH" should read -- ROH+y(CH_2CH_2O)+z($CH_3C_2H_3O$)-R(OC_nH_{2n})$_x$OH --. Column 15, line 16, "yield" should read -- yielded --. Column 19, line 54, after "compounds" insert -- from the group consisting of amines, amine salts and fatty imidazoline salts --.

Signed and sealed this 21st day of April 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents