

1

2,820,007

LUBRICATING COMPOSITIONS

Johan Leonard Van Der Minne and Pieter Hendrik Jan Hermanie, Amsterdam, Netherlands, assignors to Shell Development Company, New York, N. Y., a corporation of Delaware

No Drawing. Application November 15, 1954
Serial No. 469,036

Claims priority, application Netherlands
November 24, 1953

3 Claims. (Cl. 252—33.3)

The present invention relates to improved water-in-oil emulsions. More particularly the present invention relates to stable water-in-oil emulsions which are applicable to various industrial uses.

The stability of water-in-oil emulsions is governed by a number of variables such as the respective amounts of the two phases, the solubility and type of emulsifier used, temperature conditions and the like. When additional components are added to one or both phases so as to render the emulsion applicable to a particular industrial function such as corrosion inhibition and lubrication of marine engine and low speed diesel engine lubrication, metal cutting emulsions, insecticidal compositions and the like, the factors governing stability of water-in-oil emulsions become more complex.

It is an object of the present invention to provide a stable water-in-oil emulsion. A further object of this invention is to provide a stable water-in-oil emulsion for industrial application such as for marine engines, low speed diesel engines, insecticidal and pharmaceutical compositions, and the like. Another object of this invention is to provide water-in-oil emulsions which are thermally stable and resistant to oxidation. A further object of this invention is to provide water-in-oil emulsions which inhibit corrosion and prevent wear. Still other objects will become apparent from the following description of the invention.

It has now been discovered that water-in-oil emulsions which are stable in storage and use can be prepared by incorporating therein a combination of two particular types of oil-soluble polyvalent metal salts of organic acids. More specifically, the two polyvalent metal salts are the polyvalent metal salts of organic sulfonic acids and polyvalent metal salts of alkylated aromatic hydroxycarboxylic acids. If desired, a third polyvalent metal salt can be added in conjunction with the two salts mentioned above which salt is a polyvalent metal phenate. When this latter salt is used it is generally used to replace a part of the polyvalent metal salt of an alkylated aromatic hydroxycarboxylic acid and should preferably be one which corresponds with respect to the metal portion of the salt to the polyvalent metal used to neutralize the alkylated aromatic hydroxycarboxylic acid.

By means of the combination of emulsifiers mentioned, the desired stability of the emulsions can be obtained even by using relatively small quantities of emulsifiers. In many cases the desired stability is obtained even by employing a quantity of emulsifiers containing together not more than 0.05–0.5% by weight of polyvalent metal, calculated on the oil phase. Larger quantities of the emulsifiers may also be used.

The ratio of the quantities of both emulsifiers may vary within wide limits. In general it may be stated that the desired stable water-in-oil emulsions are obtained when the weight ratios of the two types of emulsifiers vary from about 95:5 to about 5:95 or from about 85:15 to about 15:85. Preferably a weight ratio lying between 60:40 and 40:60 is used.

2

The sulfonates can be neutral and/or basic oil-soluble sulfonates derived from any suitable material and prepared by any of the well-known suitable methods. Preferred materials for making oil-soluble sulfonates include petroleum fractions, alkyl substituted aromatic compounds and alkyl substituted polar containing aromatic compounds. The petroleum sulfonates suitable for use in compositions of this invention are described in United States Patents 2,361,804, 2,480,638, 2,485,861, 2,509,863, 2,501,731 and 2,585,520. If desired, the sulfonates can be purified by the methods described in United States Patents 2,441,258 and 2,488,721. The aromatic sulfonates which can be utilized in compositions of this invention include those described in United States Patents 2,411,583, 2,418,894, 2,442,915, 2,556,108 and 2,556,848. Although various polyvalent metal sulfonates are contemplated in the practice of the invention, including alkaline earth metal organic sulfonates (including magnesium) and other polyvalent metal organic sulfonates, particularly other divalent metal organic sulfonates and trivalent metal organic sulfonates, the sulfonates of the metals of group II of the periodic table and having an atomic number from 12 to 56 are preferred, and especially of the alkaline earth metals within that group of metals. Specific sulfonates which are particularly suitable for use in compositions of this invention include oil-soluble metal sulfonates such as Ca, Ba, Mg, Zn, Al, Cd, Sn, Cr and Co petroleum sulfonate, tetra-tertiary butylnaphthalene sulfonate, diwaxbenzene sulfonate, stearylbenzene sulfonate, diwaxnaphthalene sulfonate, diisobutylenephene sulfonate, tertiaryoctylphenol sulfonate, ditertiaryamylphenol sulfonate, alkylated dibenzothiophene sulfonate and mixtures thereof.

The other emulsifier component can be a neutral, inner or basic oil-soluble polyvalent metal salt of an alkylated aromatic hydroxy carboxylic acid in which the alkyl groups should contain at least 5 and preferably 12–18 carbon atoms. The number of alkyl groups in the aromatic hydroxycarboxylic acids from which the present emulsifier component is derived, is preferably 1 or 2.

The alkylated aromatic hydroxy carboxylic acids can be prepared by any convenient method such as described in U. S. Patents 1,998,750 and 2,490,444 and converted to the polyvalent metal salt by the method described in U. S. Patents 2,253,811 and 2,293,419. Still another method of preparing the polyvalent metal salicylates is to treat the carboxylated alkyl phenates as prepared by the method described in U. S. Patent 2,685,600 with calcium chloride, oxide, hydroxide or mixtures thereof. Instead of the calcium salts other alkaline earth metal chlorides, oxides or hydroxides can be used as well as the corresponding zinc, cadmium, lead, nickel or other polyvalent metal compounds.

The salt of the alkylated aromatic hydroxycarboxylic acid need not be pure but may be admixed with a polyvalent metal salt of an alkyl phenol which contains no other acetic group. For the purpose of the invention, it is very suitable to use, for example, a mixture of polyvalent metal salts of alkyl salicylic acids and alkylphenol obtained by reacting alkali metal alkylphenates with carbon dioxide according to the Kolbe-Schmidt method, whereby a large part of the phenate is converted into salicylate, and by treating the resultant mixture with an inorganic salt of a polyvalent metal as well as with an oxide or hydroxide of the polyvalent metal. In this manner, a basic salicylate of a polyvalent metal can be obtained which is mixed with a minor quantity of a corresponding polyvalent metal alkylphenate. The use of such basic mixtures as emulsifiers has its advantages for certain applications. It has been found that the stability of water-in-oil emulsions is usually promoted by higher basicity of the emulsifier. The basicity of the mixtures

of polyvalent metal alkylsalicylates and polyvalent metal alkylphenates can be further increased by not immediately reacting the product, obtained after treating the alkali metal alkylphenate with carbon dioxide according to the Kolbe-Schmidt method, with an inorganic salt of a polyvalent metal and an oxide or hydroxide of the polyvalent metal, but by first treating the product referred to with an alkali metal, an alkali metal hydroxide or an alkali metal alcoholate, if desired followed by a second treatment with carbon dioxide according to the Kolbe-Schmidt method which in turn may be followed by a fresh treatment with an alkali metal, an alkali metal hydroxide or an alkali metal alcoholate.

The lubricating oil used to form the water-in-oil emulsion of this invention can be any natural or synthetic hydrocarbonaceous oil having lubricating properties. Thus, the base may be a hydrocarbon oil of wide viscosity range, e. g., 100 SUS at 100° F. to 150 SUS at 210° F. The hydrocarbon oils may be blended with fixed oils such as castor oil, lard oil and the like, and/or with synthetic lubricants such as polymerized olefins, copolymers of alkylene glycols and oxides; organic esters of polybasic organic and inorganic acids, e. g., di-2-ethylhexyl sebacate, dioctyl phthalate, trioctyl phosphate; polymeric tetrahydrofuran; polyalkyl silicone polymers, e. g., dimethyl silicone polymer and the like.

Representative mineral lubricating oils which have been utilized in evaluating the utility of the present additives had the following specifications:

Gravity, ° API	Min. 26.5	Min. 24.5.
Pour point, ° F	Max. 10	Max. -5.
Flash, C.C. ° F	Min. 490.	Min. 415.
Viscosity, SUS, at 210° F	120-125	60-65.
Viscosity index	Min. 95.	50-60.

The ratio of the quantity of the water phase to the quantity of the oil phase in the emulsions used may vary within wide limits. Generally any ratio may be used which leads to an emulsion of the water-in-oil type.

This good industrial lubricating emulsion can be produced by admixing about one part of the non-aqueous phase of the emulsion with from 2 to 50 and preferably with from 5 to 25 parts of water.

The water-in-oil emulsions can be prepared by any of the usual methods. In general the preparation is best carried out by adding the emulsifiers to the oil, after which the water phase is added and the mixture stirred, if desired followed by a further homogenizing treatment which may for instance, be carried out by passing the emulsion through a gear pump. This latter operation permits the average size of the dispersed particles in the emulsion to be considerably decreased, for example to an average size of 2 microns or less.

If desired, one or more other emulsifiers can be used in addition to the emulsifiers of the two types mentioned, provided the effect obtained with the combination of the emulsifiers described is not nullified and there is compatibility among the various constituents making up the final product.

The use of the combination of emulsifiers described is not only important to the preparation of water-in-oil emulsions of which the aqueous phase is pure or practically pure water, but also for the preparation of water-in-oil emulsions of which the aqueous phase contains dissolved products such as water-soluble electrolytes. Water-in-oil emulsions of which the water phase contains a salt of a divalent metal in a quantity of at least 0.05 mol per liter, preferably more than 0.25 or 0.5 mol per liter, are particularly suitable for lubricating internal combustion engines, especially diesel engines, which are run on a fuel having a sulfur content of at least 0.01% by weight, particularly at least 0.1% by weight, calculated as elemental sulfur. Especially calcium, barium, magnesium, and zinc salts of the lower fatty acids of from 1 to 4 carbon atoms,

particularly formates, acetates and propionates, come into consideration.

Furthermore, water-in-oil emulsions of which the aqueous phase contains, e. g., potassium carbonate or calcium hydroxide are suitable for lubricating cylinders of steam engines.

The invention will be illustrated by the following example.

As the polyvalent metal salt of an organic sulfonic acid a basic calcium salt of a petroleum sulfonic acid was used. The petroleum sulfonic acid was obtained by treating a lubricating oil distillate, which was free from naphthenic acids and had been extracted with furfural, firstly with 5% by weight of concentrated sulfuric acid and then with 35% by weight of oleum, and extracting from the sulfonation product, after the removal of the acid sludge, the oil-soluble sulfonic acids. This emulsifier component will be further designated by the letter A.

As the polyvalent metal salt of an aromatic hydroxycarboxylic acid a mixture of a major amount of basic calcium alkyl salicylates, of which the alkyl groups have a straight chain of 14-18 carbon atoms, and a minor amount of calcium C₁₄₋₁₈ alkyl phenates was used. The salicylates and the phenates contained 1-2 alkyl groups, i. e., part of the molecules contained one and the remaining molecules two alkyl groups each. This mixture was obtained by reacting a mixture of sodium alkyl phenates having 1-2 essentially normal alkyl groups of 14-18 carbon atoms, with carbon dioxide according to the Kolbe-Schmidt method, treating the resultant product with sodium hydroxide and then reacting it again with carbon dioxide according to the Kolbe-Schmidt method, and subsequently reacting the product with calcium chloride and calcium oxide. The resultant product had a basicity of 213% wherein "basicity" is defined as follows: If the actual calcium content of the product is *a*%, and the theoretical calcium content, when the calcium is present only in the form of neutral calcium alkyl-salicylates (with free phenol hydroxyl group) is *b*%, the percentage basicity of the product is given by

$$\frac{a-b}{b} \times 100$$

This emulsifier component will hereinafter be referred to as B.

The three emulsions were prepared, viz.

- (1) A water-in-oil emulsion, using only emulsifier A;
- (2) A water-in-oil emulsion using only emulsifier B;
- (3) A water-in-oil emulsion using a combination of

emulsifier A and emulsifier B.

The various emulsions were prepared by adding the emulsifier or emulsifiers to a lubricating oil distillate which had been extracted according to the Edeleanu process and which had a viscosity of 42 centistokes at 60° C. In the preparation of emulsion No. 1 a quantity of emulsifier A was used corresponding to 0.4% by weight of calcium, calculated on the lubricating oil distillate. In the preparation of emulsion No. 2 the emulsifier B was also used in a quantity corresponding to 0.4% by weight of calcium, calculated on the lubricating oil distillate. Finally, in preparing emulsion No. 3 emulsifiers A and B were used in quantities corresponding to 0.2% by weight each of calcium, calculated on the lubricating oil distillate.

In each of the three cases a quantity of 30 parts by volume of an 18% calcium acetate solution in water was emulsified by stirring into 70 parts by volume of the lubricating oil distillate, after which the emulsion was passed through an emulsifying apparatus for further homogenizing. The emulsions were then allowed to stand, after which the following observations were made:

- | | |
|--|--|
| Emulsion No. 1, prepared with emulsifier A. | The emulsion showed pronounced flocculation after 12 days. |
| Emulsion No. 2 prepared with emulsifier B. | The emulsion showed pronounced flocculation after 12 days. |
| Emulsion No. 3 prepared with a combination of emulsifier A and emulsifier B. | The emulsion showed no flocculation at all even after six weeks. |

From the results obtained it appears that when the combination of the emulsifiers of the invention is employed, a water-in-oil emulsion is obtained which is much more stable than the corresponding water-in-oil emulsions, in which only one of the two emulsifiers is present.

When using a combination of emulsifier A with emulsifier B each in a quantity corresponding to only 0.05% by weight of calcium, based on the oil, it was also found that even after six weeks the resultant emulsion showed no flocculation.

Water-in-oil emulsions of this invention, in addition to being stable, can be used as bases for cutting fluids, corrosion inhibiting compositions, insecticidal compositions, steam cylinder lubricants and base lubricants for various marine installations.

In the present specification, the term stability denotes not only the property of the emulsion of not separating water, but also the property of not separating oil. The drops of water in most water-in-oil emulsions have a tendency to flocculate which means that after certain time they adhere to each other. In this way flocks are formed in which the separate water drops are still present. The sedimentation velocity of these flocks, however, is considerably larger than that of the separate water drops and the consequence is that a layer of free oil is formed. This is a distinct drawback for various industrial applications and necessitates stirring before use. In practice this stirring may be very cumbersome. According to the invention, emulsions may be made in which the tendency of the water drops to adhere to each other is eliminated, in other words they are peptized. As a consequence, no flocculation occurs and no separation of oil takes place. Stirring before use is therefore not necessary, or only to a minor degree.

We claim as our invention:

1. A stable water-in-mineral oil emulsion composition

consisting essentially of at least 25% water and the balance being mineral oil containing totally from 0.05% to 0.5% by weight of calcium calculated on the oil phase of an additive combination of an oil-soluble basic calcium petroleum sulfonate and an oil-soluble basic calcium C₁₂₋₁₈ alkylsalicylate, the water phase of the emulsion being free of water-soluble inorganic metal salts.

2. A stable water-in-mineral oil emulsion composition consisting essentially of 30% water and 70% mineral oil, said emulsion containing totally from 0.05% to 0.5% by weight of calcium calculated on the oil phase of an additive combination in the weight ratio of from 95:5 to 5:95 of oil-soluble basic calcium petroleum sulfonate and basic calcium C₁₄₋₁₈ alkyl salicylate, the water phase of the emulsion being free of water-soluble inorganic metal salts.

3. A stable water-in-mineral oil emulsion composition consisting essentially of 30% water and 70% mineral oil containing 0.2% Ca as basic calcium petroleum sulfonate and 0.2% Ca as basic calcium C₁₄₋₁₈ alkyl salicylate each calculated on the oil phase, the water phase of the emulsion being free of water-soluble inorganic metal salts.

References Cited in the file of this patent

UNITED STATES PATENTS

2,231,168	Lazar	Feb. 11, 1941
2,305,560	Schiermeier	Dec. 15, 1942
2,322,822	Brown	June 29, 1943
2,372,411	Van Ess	Mar. 27, 1945
2,425,174	Carmichael	Aug. 5, 1947
2,606,872	Gasser et al.	Aug. 12, 1952
2,606,874	Garner	Aug. 12, 1952
2,671,758	Vinograd	Mar. 9, 1954
2,744,870	Stillebroer et al.	May 8, 1956