United States Patent Office 2,852,353 Patented Sept. 16, 1958

2,852,353

DISTILLATE FUEL OILS INHIBITED AGAINST HAZE FORMATION

Wilmot W. Craig, Swarthmore, and Earl E. Fisher, Glenolden, Pa., assignors to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application June 4, 1954
Serial No. 434,641

1 Claim. (Cl. 44—56)

This invention relates to distillate fuel oils inhibited against haze formation.

Fuel oil distillates of the type utilized in domestic heating oils, diesel fuels and the like, tend to take up small amounts of water during distillation, shipping and/or storage. When distillate fuel oils containing appreciable water concentrations are subjected to temperature variations, they tend to develop a hazy appearance owing to the formation of emulsions or dispersions having water particles of relatively large size in the dispersed phase. These emulsions or dispersions tend toward instability on standing. Because of this lack of stability the dispersed water particles tend to coalesce, settle out and form accumulations of appreciable magnitude. For this reason, rust, corrosion and/or problems in the maintenance of storage or combustion facilities often follow from the use of hazed fuel oils.

The present invention is directed to inhibiting the development of haze in distillate fuel oils, and more particularly to fuel oils containing at least 0.025 percent by volume of a haze inhibiting composition formed by admixture of from about 1.25 to about 15 percent by weight of an alkanol amine selected from the group consisting of primary, secondary and tertiary alkanol amines whose alkanol substituents contain from 2 to 3 carbon atoms, from about 3.75 to about 45 percent by weight of a fatty acid containing from 12 to 24 carbon atoms, the fatty acid:alkanol amine mol ratio being in excess of 1:1, from about 0.1 to about 3 percent by weight of an amine salt of a primary, aliphatic amine containing from 8 to 18 carbon atoms and a dialkyl orthophosphoric acid, the alkyl substituents of which contain from 3 to 10 carbon atoms, from about 0.9 to about 22 percent by weight of an alkali metal salt of an oil-soluble sulfonic acid and from about 15 to about 94 percent by weight of a coupling agent selected from the group consisting of butanol, 2-butoxyethanol and diethylene glycol monobutyl ether.

The herein disclosed haze inhibiting compositions function to promote a "bright" or transparent appearance in fuel oils over a range of temperatures that is substantially greater than would be possible without benefit of the invention. This function is accomplished by the formation of a water-oil solution or dispersion wherein the dissolved or dispersed aqueous particles are maintained in extremely small size (normally less than about 0.05 μ), notwithstanding relatively extreme temperature conditions and notwithstanding relatively large water concentrations. Such solutions or dispersions are relatively stable and show little tendency to stratify. Although the exact manner of functioning of the individual components of the composition is not fully understood because of the present undeveloped state of emulsion technology, it can be said that the components interact in the proportions indicated and provide the necessary hydrophilic-lipophilic balance required to impart homogeneity and a high degree of stability to distillate fuel oils containing water, over a wide range of temperatures, even when the haze inhibiting compositions are used in extremely small concentrations.

The term "solution" is used herein in its normal broad sense to include colloidal solutions or emulsions as well as true solutions.

The haze inhibiting compositions of this invention may be prepared by blending the components thereof in any order and in the ratio indicated. Although it is normally desirable directly to blend the components of the composition at room temperature, it is sometimes preferred to expedite the preparation of the composition by effecting admixture of the components at an elevated temperature below the boiling point of the lowest boiling component of the mixture, and/or through the expedient of utilizing previously formed solutions of the individual components in a mineral oil base. Taking up the components of the composition in detail, the composition has incorporated therein from about 1.25 to about 15 percent by weight of a primary, secondary or tertiary alkanol amine whose alkanol substituents contain from 2 to 3 carbon atoms. Examples of alkanol amines included by the invention are monoethanol amine, diethanol amine, triethanol amine and diisopropanol amine. The alkanol amine is considered to react with the excess of fatty acid that is incorporated in the composition to form, in situ, an alkanol amine soap, of which triethanol amine oleate and stearate are illustrative. Although these alkanol amine soaps possess appreciable lipophilic properties, the hydrophilic properties imparted to the soap by the alkanol substituents tend to predominate. The alkanol amine soap functions in the composition as an emulsifying agent and forms a substantial portion of the composition.

The haze inhibiting composition additionally has incorporated therein from about 3.75 to about 45 percent by weight of a fatty acid containing from 12 to 24 carbon atoms per molecule. The concentration of the fatty acid is such as to provide a fatty acid:alkanol amine mol ratio in excess of 1:1. Particularly effective compositions are produced when the fatty acid:alkanol amine mol ratio is between about 1:1 and about 1:3. Examples of fatty acids included by the invention are n-dodecanoic acid, stearic acid, oleic acid, linoleic acid and tetracosanoic acid. Fatty acids which are liquid at room temperature, such as oleic acid, are preferred in order to facilitate blending at room temperature. However, as heretofore indicated blending at room temperature of normally solid fatty acids may be expedited by previously dissolving the same in a small amount of a mineral oil solvent. The free fatty acid functions in the composition as a lipophilic co-emulsifier and stabilizing agent.

The haze inhibiting composition further contains from about 0.9 to about 22 percent by weight of an alkali metal salt of an oil-soluble sulfonic acid. Particularly effective compositions are produced when the alkali metal sulfonate is incorporated in the composition in an amount sufficient to provide a sulfonate: alkanol amine mol ratio between about 0.4:1 to about 0.8:1. The class of alkali metal salts of oil-soluble sulfonic acids is well-known and includes salts of aliphatic hydrocarbon sulfonic acids containing at least 8 carbon atoms per molecule, and alkyl substituted aromatic hydrocarbon sulfonic acids whose substituents contain at least 8 carbon atoms. Examples of such acids are the higher molecular weight naphthene sulfonic acids and the higher molecular weight alkyl benzene sulfonic acids, such as the wax alkyl benzene sulfonates. Commercial mixtures of alkali metal salts of oil-soluble hydrocarbon sulfonic acids, such as sodium petroleum sulfonate, are especially suitable for the purposes of this invention. Such salts have average molecular weights ranging from about 450 to about 650 and are prepared by neutralization of petroleum sulfonic acids resulting from sulfuric acid treatment of lubricating oil distillates. These salts and their preparation are known in the art and need not be discussed in detail. The alkali

metal hydrocarbon sulfonate functions in the composition as a co-emulsifying agent of extremely hydrophilic characteristics. The herein disclosed sulfonates also act as solubilizing agents for the alkanol amine soaps, maintaining a high degree of solubility for the latter over a wide range of temperatures. These compounds also impart rust inhibiting properties to the composition.

The haze inhibiting composition further contains from about 0.1 to about 3 percent by weight of an amine salt of a primary aliphatic amine containing from 8 to 18 carbon atoms per molecule and a dialkyl orthophosphoric acid, the alkyl substituents of which contain from 3 to 10 carbon atoms. Particularly effective compositions are produced when the amine salt:alkanol amine mol ratio is between about 0.04:1 and about 0.08:1. Representative examples of amine salts included by the invention are n-octyl, n-dodecyl, n-octadecyl and n-octadecenyl amine salts of di-n-propyl, di-n-amyl, di-n-capryl, and isoamyl isooctyl orthophosphoric acids. The amine salts of commercial amine mixtures, such as cocoamine, a mixture containing predominantly lauryl amine together with lesser amounts of homologous alkyl amines containing from 8 to 18 carbon atoms per molecule, are suitable for the purposes of this invention. This component functions in the composition as a rust inhibitor, having strongly lipophilic characteristics. The amine salts, or alkyl-ammonium dialkyl orthophosphates, also possess surface active properties and contribute to the stability of water-containing fuel oils having the haze inhibiting composition of this invention incorporated therein.

The composition further contains from about 15 to about 94 percent by weight of a coupling agent or common solvent for oil and water selected from the group consisting of butanol, 2-butoxyethanol and diethylene glycol monobutyl ether. The foregoing compounds have both hydrophilic and lipophilic properties due to the presence of influential hydroxyl and butyl groups in the molecule. Particularly effective results are obtained when the coupling agent is incorporated in the composition in an amount sufficient to furnish a coupling agent:alkanol amine mol ratio of from about 3:1 to about 14:1. The coupling agent improves the miscibility of the water and the oil and increases the haze-free tolerance of the ultimate fuel oil composition for water at all temperatures.

Haze inhibiting compositions containing the foregoing components in the proportions indicated are useful when incorporated in distillate fuel oils that tend to develop haze upon admixture with water. The inhibiting compositions are remarkably effective when used in amounts of at least 0.025 percent by volume. In such concentrations, the compositions of this invention impart stability to the water-oil solution over a wide range of temperatures. Haze inhibiting compositions having a greater effect per unit quantity may be obtained by reducing the proportion of the coupling agent in the composition and correspondingly increasing the concentrations of the other components. Although the primary function of the herein disclosed composition is to inhibit haze formation in fuel oils tending to develop the same when admixed with small amounts of water, the increased affinity for water imparted to fuel oils by the present compositions is additionally advantageous in that continued use of fuel oils containing the inhibitor composition of this invention will also reduce and/or eliminate previous accumulations of water that have developed in a given installation from the use of less stable, water-containing fuel oils.

As indicated, the fuel oils to which the compositions of this invention may be added include those distillate fuel oils tending to form haze when admixed with small amounts of water, and these oils may either consist entirely of straight-run fuel oil distillate, or alternatively, they may contain catalytically cracked fuel oil distillate, alone, or in admixture with straight-run fuel oil distillate.

The utility of the herein disclosed haze inhibiting compositions is illustrated by the following specific embodiments of the invention.

EXAMPLE I

Two compositions, composition A and composition B, were made up by admixture of the following components in the proportions indicated at room temperature with stirring:

Composition	A	B
Agent, Percent by Wt.:		
Butanol	37.8	
2-Butoxyethanol		37.8
Sodium Salt of Oil-Soluble Petroleum Sulfonic Acids prepared by the neutralization of Petroleum Sulfonic Acids resulting from sulfuric acid treatment of lubricating oil distillates and having an average molecular weight of approximately 450	17.7	17.7
Cocoamine Salt of 3-Methylbutyl, 2-Ethylhexyl o-Phosphoric Acid (84% Solution)	1.7	1.7
Oleic Acid	34.0	34.0
Triethanol Amine	8.8	8.8

Each of compositions A and B was incorporated in varying amounts in samples of a typical, commercial No. 2 fuel oil containing both straight-run and catalytically cracked distillates, having a gravity of 34.8° API and a water content (Karl Fischer method) of 246 parts per million, in order to demonstrate the haze inhibiting effect thereof. The haze point for the fuel oil was determined by heating the fuel oil until it became bright, or transparent, and then cooling until a haze appeared. The haze point is that temperature at which a haze appears. The effect of each of compositions A and B upon the haze point of the fuel oil is demonstrated in the results set forth in the following table:

Table 1

Run No.	1	2	3	4	5	6	7
Additive Concentration, Percent by Vol.		0.001	0.01	0.02	0.03	0.04	0.05
Fuel Oil plus Composition A, Haze Point, ° F.	89	82	79	76	63	43	4
Fuel Oil plus Composition B, Haze Point, ° F.	89	83	76	72	62	48	10

As evidenced by the foregoing data the herein disclosed haze inhibitors are effective in extremely small proportions to promote a stable solution of water in distillate fuel oils over a wider range of temperatures than is possible without benefit of the invention. It is particularly noted that the haze point reduction per unit of the composition added is exceptional, when the composition is present in the fuel oil in excess of 0.025 percent by volume. Other similarly effective, haze inhibiting compositions can be obtained by admixture of other of the herein disclosed components, either in the proportions indicated in the foregoing specific embodiments, or in other proportions disclosed herein as substantially equivalent thereto.

Although a principal purpose of the compositions of this invention is to inhibit development of haze in distillate fuel oils, the compositions are considered to produce additionally desirable results with respect to inhibiting sludge deposition and rust or corrosion of metal surfaces with which fuel oils come into contact.

It is contemplated that the fuel oils of this invention may have added thereto, in addition to the herein disclosed haze inhibiting compositions, other improvement agents, including for example, combustion improvers, ignition quality improvers, cetane number improvers, sludge inhibitors, color stabilizers, and the like.

Numerous modifications of the herein disclosed invention may be resorted to without departing from the spirit thereof. Accordingly, the invention is limited only by the scope of the claim appended hereto.

We claim:

A distillate fuel oil normally tending to develop haze when water is present therein, and having incorporated therein a minor, haze inhibiting amount of at least about 0.025 percent by volume of a composition prepared by admixture of from about 1.25 to about 15 percent by weight of triethanolamine, from about 3.75 to about 45 percent by weight of oleic acid, the oleic acid:triethanolamine mol ratio being in excess of 1:1, from about 0.1 to about 3 percent by weight of the cocoamine salt of 3-methylbutyl,2-ethylhexyl orthophosphoric acid, from about 0.9 to about 22 percent by weight of sodium salt of oil-soluble petroleum sulfonic acids and from about 15 to about 94 percent by weight of butanol.

References Cited in the file of this patent

UNITED STATES PATENTS

2,297,114	Thompson	Sept. 29, 1942
2,527,987	Caron et al.	Oct. 31, 1950
2,550,981	Eberz	May 1, 1951
2,550,982	Eberz	May 1, 1951
2,728,643	Vaughn	Dec. 27, 1955
2,791,495	Rudel et al.	May 7, 1957

OTHER REFERENCES

"Industrial and Engineering Chemistry," vol. 41, January 1949, pp. 137–144.