Patented June 9, 1953 2,641,538

UNITED STATES PATENT OFFICE

2,641,538

PREVENTING DISCOLORATION OF FUEL OILS

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No Drawing. Application April 6, 1950, Serial No. 154,438

8 Claims. (Cl. 44—63)

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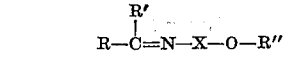
This invention relates to a novel method of preventing discoloration of fuel oils and more particularly to the use of a particular additive in fuel oils to prevent discoloration thereof.

The fuel oils to which the present application is directed, in general, comprise hydrocarbon distillates boiling above the range of gasoline and thus include particularly kerosene, #1 fuel oil, #2 fuel oil, burner oil, diesel oil, etc., as well as compositions containing these oils, such as jet fuels, tractor fuels, etc. These oils in storage tend to undergo discoloration and turn from a light to a dark color. Most consumers object to the dark colored oils and, therefore, will not purchase the discolored oils at the premium price normally prevalent for the light colored oils. In fact, some of the specifications for these oils include a minimum color requirement which the darkened oils cannot meet.

In one embodiment the present invention relates to a method of preventing the discoloration of fuel oil which comprises adding thereto the condensation product of a cyclic and more particularly a cyclic carbonyl compound and an alkanol amine.

In a specific embodiment the present invention relates to a method of preventing discoloration of fuel oil which comprises adding thereto from about 0.0005% to about 0.1% by weight of the condensation product of benzaldehyde and propanol amine.

The additives of the present invention are illustrated by the following general structure:



where R is selected from an aryl group and an unsaturated heterocyclic ring containing as the hetero atom an element selected from oxygen, sulfur and nitrogen; R′ is selected from hydrogen and a hydrocarbon group; X is selected from an alkylene and an arylene group; and R″ is selected from hydrogen and a hydrocarbon group.

Referring to the structure hereinbefore set forth, it is preferred that R comprise an aryl group. While the aryl group may contain one or more substituents attached thereto, it is particularly preferred that the substituents do not comprise a polar group because it has been found that oxygen, sulfur or nitrogen-containing groups decrease the solubility of the additive in fuel oil and, therefore, interferes with the effective use of these additives. On the other hand, the substitution of an alkyl group or groups on the aryl ring is satisfactory and, in some cases, desirable because these groups will enhance solubility of the additive in the fuel oil.

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Other R groups included within the scope of the present invention comprise an unsaturated heterocyclic ring containing oxygen, sulfur or nitrogen in the ring. Included within this class are groups such as the furan, thiophene, pyrrole, pyridine, quinoline, etc. as well as compounds containing this configuration such as coumarone, benzothiophene, indole, quinoline, etc.

The preferred compounds are readily prepared by the condensation of benzaldehyde with an alkanol amine. The alkanol amine preferably contains from 2 to about 12 carbon atoms per molecule and thus includes ethanol amine, propanol amine, butanol amine, pentanol amine, hexanol amine, heptanol amine, octanol amine, nonanol amine, decanol amine, undecanol amine and dodecanol amine. It is preferred that the amino group and the hydroxyl group are attached to adjacent carbon atoms. This is readily obtained with ethanol amine, isopropanol amine (2 - hydroxy - propyl amine), 2 - hydroxy - butyl amine, 1-amino-2-hydroxy-2-methyl-propane, 1-amino-2-hydroxy-2-methyl-butane, 2-hydroxy-pentyl amine, 5-amino-4-octanol, etc.

The condensation of benzaldehyde with an alkanol amine is readily effected at room temperature by commingling the two reactants, preferably with stirring. The reaction is exothermic and, when desired, means may be provided to cool the reaction and absorb the heat thereof. The product then may be treated in any manner to separate the water of reaction from the desired condensation product, and this may be accomplished by distillation under vacuum, azeotropic distillation in the presence of a hydrocarbon solvent, solvent extraction with a hydrocarbon such as benzene under liquid phase to form two layers, separating the aqueous layer and subsequently distilling the benzene from the desired condensation product. It is understood that any suitable method of preparing these compounds is included within the scope of the present invention.

The preferred compounds prepared in the manner hereinbefore set forth include benzalaminoethanol, benzalaminopropanol, benzalaminobutanol, benzalaminopentanol, etc., the preferred additives preferably contain from about 9 to about 20 carbon atoms per molecule. As hereinbefore set forth, when desired the aryl ring may contain hydrocarbon groups attached thereto and particularly alkyl groups.

When the cyclic group comprises an unsaturated heterocyclic ring as hereinbefore set forth, the desired additive may be prepared by the con-

densation of the corresponding aldehyde with an alkanol amine. Thus, furfural may be condensed with the alkanol amine under substantially the same conditions as hereinbefore set forth. It is understood that other suitable methods of preparing the desired product may be employed in accordance with the present invention. However, it is understood that the additives prepared in this manner are not necessarily equivalent to those prepared from an aromatic aldehyde.

The additives of the present invention and particularly those prepared from benzaldehyde offer numerous advantages over other additives for this purpose. The additives of the present invention are comparatively low in cost, being prepared from rather cheap starting materials. Further, these additives are readily soluble in fuel oils and are not readily extracted by caustic or water.

The additives of the present invention are added to fuel oils in amounts of less than about 1% and preferably in an amount of from about 0.0005% to about 0.1% by weight. It is understood that these additives may be used in conjunction with other additives, such as metal deactivators, antioxidants and preferably antioxidants of the phenolic type, synergists, cetane improvers, additives which are incorporated for improving burning properties of the oil, etc.

Fuel oils at the present time are generally obtained from two major sources. One of these sources comprises the non-destructive distillation of petroleum oil and the fuel oil so obtained is generally referred to in the art as straight run or virgin fuel oil. The other major source is from catalytic and non-catalytic cracking processes and these fuel oils are generally referred to in the art as cycle stocks. The term "cycle stock" is used because the fuel oil is separated from a fraction which is recycled to the cracking process for further conversion therein. Many commercial fuel oils comprise a mixture of virgin oil and cycle stock. In the past, fuel oils have come mostly from virgin distillates but, with the increasing amount of catalytic cracking processes being installed, a considerable quantity of catalytic cycle stock is available and is being used for fuel oil. The properties of the fuel oils vary considerably depending upon the source of the original crude oil and this difference in properties is carried through to the cycle stocks. Further, blends of the virgin and cycle stocks appear to undergo discoloration to a greater extent than the unblended oils, and the present invention is, therefore, particularly advantageous for use with the blended oils.

In view of the difference in properties of the various oils, their response to the additives of the present invention will accordingly vary. However, all of these oils will be improved by treatment with the additive of the present invention. Further, while these oils will vary considerably among themselves, they vary more so from gasoline and other lighter products insofar as response to additives is concerned. Thus, certain inhibitors which are used in gasoline and effectively serve to retard deterioration thereof will be of no value and in some cases even may be harmful when utilized in fuel oils. Thus, for example, when 0.02% by weight α-naphthol or pyrogallol was added to a fuel oil blend of virgin and catalytic cycle stocks, sediment formation increased over double over those obtained in the absence of added material. α-naphthol and pyrogallol are generally considered as satisfactory gasoline inhibitors but in the case of fuel oils they actually proved harmful. Similarly, a metal deactivator comprising disalicylalpropylene diamine, when added to another sample of the fuel oil blend mentioned above, was ineffective to retard sediment formation in the fuel oil. The same general conclusions are applied to the discoloration of fuel oils and it definitely has been established that there is no correlation between the use of certain compounds in gasoline as compared to their use in fuel oil.

As hereinbefore set forth, the properties of fuel oils vary considerably and, when confronted with a fuel oil which does not seem to be particularly responsive to the application of additives, it may be desirable to subject the fuel oil to a preliminary treatment such as with caustic acid, clay treating, etc. Such treatments have proved beneficial in improving the properties of the fuel oil to respond to the application of additives, and it is within the scope of the present invention to employ such treatments in conjunction with the application of the additives herein set forth.

The following examples are introduced to illustrate the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

The fuel oil used in this example was a typical #2 fuel oil comprising catalytic cycle stock resulting from the cracking of Mid-Continent oil. The fuel oil had an A. P. I. gravity at 60° F. of 30.3, an initial boiling point of 422° F. and an end boiling point of 603° F.

Discoloration of the fuel oil was determined in an accelerated test in which a sample of the fuel oil is placed in a constant temperature oil bath maintained at 212° F. and the color determined after 20 hours. The color was determined by the A. S. T. M. Photoelectric Color Method as described in the A. S. T. M. Standards on Petroleum Products and Lubricants, page 615, October 1947 edition.

The additive used in this example was benzalaminopropanol prepared in the manner hereinbefore set forth. 0.03% by weight of the additive was added to the fuel oil, and the results of these tests are shown in the following table. Before the test the fuel oil had a color index of 93.

Table 1

Additive	A. S. T. M. Photoelectric Color Index
None	15
0.03% benzalaminopropanol	60.6

It will be noted from the data in the above table that the benzalaminopropanol served to retard discoloration of the fuel oil to a considerable extent.

EXAMPLE II

The fuel oil used in this example was a typical #2 fuel oil and had a boiling range of from about 460° F. to about 620° F. This fuel oil was subjected to caustic washing prior to the addition of benzalaminopropanol, and the samples were tested in the manner hereinbefore set forth. The

results of these tests are shown in the following table:

Table 2

Additive	A. S. T. M. Photoelectric Color Index
None	12
0.01% by weight of benzalaminopropanol	75

Here again it will be noted that the benzalaminopropanol served to retard discoloration to a considerable extent, and also that the caustic treatment improved the response of the fuel oil to treatment with the additive.

EXAMPLE III

The additive used in this example comprised furfuralaminoethanol. The fuel oil used in this example was a typical #2 fuel oil and comprised a blend of 75% of catalytic cycle stock and 25% of virgin gas oil from a Mid-Continent crude. Different samples of the fuel oil were stored at 100° F. for 111 days, and the results of these storage tests are shown in the following table:

Table 3

Additive	A. S. T. M. Photoelectric Color Index
None	60. 5
About 0.01% by weight of furfuralaminoethanol	88

It will be noted from the data in the above table that the furfuralaminoethanol also served to retard discoloration to a considerable extent.

EXAMPLE IV

This example shows the superiority of the condensation products of the present invention over aliphatic amino hydroxy compounds as typified by 5-amino-4-octanol. In a series of storage tests of samples of the blend described in Example III, the following results were obtained with various additives.

Table 4

Additive	A. S. T. M. Photoelectric Color Index	Insoluble Gum Mg./ 100 ml.
None, after 81 days	64. 5	3. 4
0.01% by weight of amino octanol, after 77 days	70. 0	0. 4
0.01% by weight of benzalaminoethanol after 77 days	90. 0	0. 7
0.01% by weight of furfuralaminoethanol after 77 days	90. 5	0. 7

It will be noted that all of the above inhibitors retarded gum formation to a considerable extent but that the benzalaminoethanol and furfuralaminoethanol retarded discoloration to a considerable extent, whereas the amino octanol did not serve to retard color formation to the extent obtained with the other additives.

EXAMPLE V

This example illustrates the effectiveness of benzalaminoethanol, prepared in accordance with the teachings of the present invention, as compared with benzylaminoethanol, prepared by reduction of the benzalaminoethanol. The fuel oil used in this example is a typical #2 fuel oil comprising a blend of 25% virgin and 75% catalytic cycle stocks from a Mid-Continent crude. Different samples of the crude containing 0.01% by weight of benzalaminoethanol and of benzylaminoethanol were stored at 100° F. for 111 days. The results of these tests are indicated in the following table:

Table 5

Additive	A. S. T. M. Photoelectric Color Index	Insoluble Gum Mg./ 100 ml.
Benzalaminoethanol	88	0. 4
Benzylaminoethanol	73	1. 1

It will be noted that the benzalaminoethanol is considerably better, both insofar as color and gum formation, than the benzylaminoethanol.

We claim as our invention:

1. A fuel oil heavier than gasoline containing, as a retarder of discoloration, a compound selected from the group consisting of a benzalaminoalkanol and a furfuralaminoalkanol, the alkanol group of said compound containing from about 2 to about 12 carbon atoms.

2. A fuel oil heavier than gasoline containing, as a retarder of discoloration, a benzalaminoalkanol in which the alkanol group contains from about 2 to about 12 carbon atoms.

3. A fuel oil heavier than gasoline containing, as a retarder of discoloration, a furfuralaminoalkanol in which the alkanol group contains from about 2 to about 12 carbon atoms.

4. A fuel oil heavier than gasoline containing, as a retarder of discoloration, benzalaminoethanol.

5. A fuel oil heavier than gasoline containing, as a retarder of discoloration, benzalaminobutanol.

6. A fuel oil heavier than gasoline containing, as a retarder of discoloration, benzalaminopentanol.

7. A fuel oil heavier than gasoline containing, as a retarder of discoloration, benzalaminopropanol.

8. A fuel oil heavier than gasoline containing, as a retarder of discoloration, furfuralaminoethanol.

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