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## PREVENTING DISCOLORATION OF FUEL OIL

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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 mixture 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 the 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 darker oils cannot meet.

The treatment of fuel oils presents a difficult problem to the refiners because of the complex composition of fuel oils. As hereinbefore set forth, fuel oils are higher boiling than gasoline and, because of the higher boiling characteristics, fuel oils contain a higher number and wider variety of different compounds. It is well known that, as the molecular weight or boiling range of a hydrocarbon distillate increases, the number of isomers of a particular boiling range and the number of different chemical structures increase. Further, fuel oils vary considerably depending upon the source of the crude petroleum; that is, the composition of fuel oils varies considerably as to the geographic source of the crude oil.

In the past, fuel oils have come primarily from non-destructive distillation of crude oils and these fuel oils are commonly referred to in the art as virgin or straight run distillates. However, due to the recent increase in cracking processes and particularly catalytic cracking processes, the use of cycle stocks from the cracking operations as fuel oil or as a component in fuel oil is increasing. 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. Fuel oils derived from cycle stocks likewise comprise a complex composition which is dependent upon the source of the original crude oil and upon whether the cracking is non-catalytic or catalytic, as well as upon the severity of the particular cracking operation employed.

Still further, present practices include blending virgin fuel oil with cycle stock to form a blended fuel oil for marketing. The blended fuel oil thus contains the complex compositions of both the virgin and cycle stocks.

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From the above description, it is apparent that the treatment of fuel oils is a difficult problem. It has been found that the use of any given additive or even a mixture of two additives, will not serve satisfactorily to retard discoloration of all or even the greater portion of virgin fuel oils from different geographic sources, of cycle stock fuel oils, or of blends of virgin and cycle stocks. The response or susceptibility of fuel oils to additives varies considerably depending upon the geographic source and the type of treatment. However, for an additive for use in fuel oils to be commercially satisfactory, it must satisfy the greater portion of commercial fuel oils regardless of the source or type of treatment. The present invention offers a novel additive mixture which will satisfy a large variety of commercial fuel oils.

It is readily appreciated that the use of an additive mixture as proposed in the present invention will find a ready acceptance in the fuel oil industry because it will accomplish results which otherwise are not obtainable. This will prove to be of great advantage to refiners who at present are facing extreme hardship in retarding discoloration of fuel oils and, therefore, are having difficulty in satisfactorily marketing their fuel oils.

In one embodiment the present invention relates to a method of retarding discoloration of a fuel oil which comprises adding thereto an additive mixture comprising (1) the condensation product of a benzaldehyde and an alkanol amine, (2) an alkanol amine, (3) an alkyl amine and (4) a metal deactivator.

In a specific embodiment the present invention relates to a method of retarding discoloration of a fuel oil which comprises adding thereto a stabilizing amount of an additive mixture comprising (1) the condensation product of a benzaldehyde, and an alkanol amine containing from about 2 to about 12 carbon atoms per molecule, (2) an alkanol amine containing from about 8 to about 40 carbon atoms per molecule, (3) an alkyl amine containing from about 6 to about 20 carbon atoms per molecule and (4) a metal deactivator.

The additive mixture of the present invention as hereinbefore set forth is adapted for use in a wide variety of fuel oils. Each of the components is necessary to the satisfactory utilization of the additive mixture because it has been found that the absence of one or more of these components destroys the capability of the additive mixture to function satisfactorily in a wide variety of fuel oils. Thus, it appears that each of the components cooperates with the other components

and is mutually dependent thereon for successful use in the manner herein intended.

The additive mixture includes the condensation product of a benzaldehyde and an alkanol amine containing from about 2 to about 12 carbon atoms per molecule. The benzaldehyde may contain alkyl substituent groups attached to the benzene mucleus but preferably does not contain a polar group (a group containing oxygen, nitrogen and/or sulfur) attached to the benzene nucleus as this substitution has been found to decrease solubility of the compound in fuel oils. On the other hand, the presence of a hydrocarbon radical on the benzene nucleus will increase solubility. The alkanol amine contains from about 2 to about 12 carbon atoms per molecule and, therefore, includes ethanol amine, propanol amine, butanol amine, hexanol amine, heptanol amine, octanol amine, nonanol amine, decanol amine, undecanol amine and dodecanol amine.

The condensation of a benzaldehyde and an alkanol amine is readily effected at room temperature by mixing of the two reactants, preferably with stirring. The reaction is exothermic and provision may be made for cooling to absorb the heat of reaction. The products are then treated by distillation, preferably under vacuum, azeotropic distillation, solvent extraction or in any suitable manner to separate the water of reaction from the desired condensation product.

The second component of the additive mixture comprises an alkanol amine containing from about 8 to about 40 carbon atoms per molecule and thus will include octanol amine, nonanol amine, etc. up to tetracontanol amine, or mixtures thereof. A particularly preferred alkanol amine for use in accordance with the present invention comprises the reaction product of ethylene oxide with an alkyl amine containing from about 10 to about 20 carbon atoms per molecule. This reaction is readily effected at room or slightly elevated temperature, and the condensation product will generally contain several ethyl hydroxyl radicals which may vary from 2 to 20 or more. In place of ethylene oxide, other suitable alkylene oxides may be employed including propylene oxide, butylene oxide, etc. In general, it is preferred that the alkanol amine contains at least one branched chain grouping per molecule and also preferably comprises a mixture of at least two different alkanol amines.

Another component of the additive mixture comprises an alkyl amine containing from about 6 to about 20 carbon atoms per molecule and thus includes hexyl amine, heptyl amine, octyl amine, etc. up to eicosanol amine or mixtures thereof. The alkyl amine preferably includes at least one branched chain grouping molecule and also preferably comprises a mixture of at least two different alkyl amines.

The next component in the additive mixture comprises a metal deactivator, which term is used to define a compound having the property of offsetting the deleterious effect of metals such as copper, vanadium, iron, cobalt, nickel, etc. to catalyze discoloration of the fuel oil. The metal deactivators are further defined as compounds capable of forming chelate compounds with the metals. A particularly preferred metal deactivator comprises the condensation product of an ortho hydroxy aromatic aldehyde with an alkylene polyamine. A particularly preferred metal deactivator is disalicylal diamino propane formed by the condensation of salicylaldehyde and propylene diamine. Another satisfactory metal deactivator comprises the condensation product of salicylaldehyde with an o-aminophenol. Still another satisfactory metal deactivator comprises the tetra sodium salt of ethylene diamine tetraacetic acid and similar compounds. In general, it is preferred that the metal deactivator does not contain more than about 25 carbon atoms per molecule.

It generally is preferred to utilize the additive mixture in a suitable solvent in order to insure complete solubility of the additive mixture in fuel oils. Any suitable solvent may be employed, including alcohols, ketones, etc. A particularly preferred solvent comprises isopropanol.

The concentrations of the various components in the additive mixture may be varied over rather a wide range but, in general, will be within the following limits: from about 10% to about 50% by weight of the condensation product of a benzaldehyde and the alkanol amine, from about 10% to about 70% by weight of the alkanol amine, from about 10% to about 70% by weight of the alkyl amine, and from about 1 to about 20% by weight of the metal deactivator. The solvent will generally be utilized in an amount of from about 10% to about 50% by weight of the additive mixture.

The additive mixture as hereinbefore set forth, will generally be satisfactory in a wide range of fuel oils. However, in some cases, it may be desirable to also include in the additive mixture an antioxidant and more particularly a phenolic antioxidant such as alkyl phenols, alkoxy phenols, alkyl-alkoxy phenols, amino phenols, naphthols, alkyl naphthols, alkoxy naphthols, alkyl hydroxy coumarans, etc. It is understood that a mixture of two or more different phenolic compounds may be employed. The phenolic compound, when employed, will generally be utilized in an amount of from about 10 to about 50% by weight of the additive mixture.

The additive mixture will be incorporated in the fuel oil in an amount of less than about 1% by weight of the fuel oil and more particularly in an amount of from about 0.0005% to about 0.1% by weight. It is understood that this additive mixture may be utilized along with other additives added for a specific purpose as, for example, when the fuel oil is to be used as diesel fuel, a cetane improver may also be incorporated in the oil.

Even with the multicomponent additive mixture of the present invention, some fuel oils may not be completely responsive to treatment therewith. In such cases, it may be desirable to first subject the fuel oil to treatment with caustic, acid and/or clay treatment, and thereafter incorporate the additive mixture to the fuel oil. Treatment in this manner has been beneficial in some cases and, therefore, is included within the scope of the present invention.

In addition to the beneficial results obtained insofar as preventing discoloration of fuel oil, it has been observed that the additive mixture of the present invention also reduces sediment formation in fuel oils and this, therefore, provides a further advantage to the novel additive mixture.

The following examples are introduced to illustrate further 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 a 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 different samples of the fuel oil were 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. This test correlates fairly well with long time storage tests as will be shown in some of the following examples.

The additives used in the following sample are as follows: (A) benzalaminopropanol formed by the condensation of benzaldehyde and isopropanol amine, (B) an alkanol amine mixture formed by the condensation of ethylene oxide with a mixture of alkyl amines containing from about 16 to about 18 carbon atoms per molecule, (C) an alkyl amine fraction comprising a mixture of alkyl amines containing from about 8 to about 14 carbon atoms per molecule, and (D) a metal deactivator comprising disalicylal diamino propane formed by the condensation of salicylaldehyde and 1,2-propylene diamine. In the interest of simplicity, these additives will be referred to in the following table according to the letters indicated above.

The additive mixture of the present invention, hereinafter referred to as E, comprised, on a weight basis, approximately 21% A, 40% B, 15% C, 4% D and 20% of a solvent comprising isopropanol.

Before the start of the accelerated test the fuel oil had an A. S. T. M. color index of 93. Different samples of the oil were tested in the accelerated test described above, with the following results: Each additive was used in an amount of 0.03% by weight.

*Table 1*

| Additive | A. S. T. M. Photoelectric Color Index |
|---|---|
| None | 15 |
| A | 66.6 |
| B | 77 |
| C | 52 |
| D | 34 |

From the above data it would appear that additive B in itself would be satisfactory to retard discoloration of the fuel oil. However, the particular sample of the fuel oil used in this example was free from metals. Upon the addition of a small amount of copper to the fuel oil, it was noted that the color index fell considerably. Therefore, another sample of the fuel oil containing metal was tested with additives B and D. This did not prove satisfactory as will be shown by the data in the following table. Also, various other combinations of additive B with the other additives were tried, and these results are also shown in the following table, as well as the results of additives A and D and of additive mixture E. Each additive was used in an amount of 0.03% by weight.



*Table 2*

| Additive | A. S. T. M. Photoelectric Color Index |
|---|---|
| B+D | 45 |
| B+A | 49 |
| A+D | 57 |
| E | 61 |

From the data in the above table, it is apparent that additive mixture E is better than the other combinations tested. As hereinbefore set forth, additive mixture E is also more desirable because of its satisfactory use in a wide variety of different fuel oils.

## EXAMPLE II

The fuel oil used in this example was a typical #2 fuel oil comprising catalytic cycle stock formed in the cracking of a West Texas oil. In this example the additives were employed in an amount of 0.05% by weight. Additive F comprised a mixed alkyl amine fraction containing primarily 12 carbon atoms per molecule and thus is comparable to previously referred to additive C. The results of the accelerated tests are given in the folowing table: Prior to the accelerated test, the fuel oil had a color index of 93.

*Table 3*

| Additive | A. S. T. M. Photoelectric Color Index |
|---|---|
| None | 22 |
| A | 13 |
| B | 6 |
| F | 3 |
| E | 66 |

It will be noted that additive mixture E in this series of tests was considerably better than any of the additives alone.

## EXAMPLE III

The fuel oil described in Example II was subjected to storage tests at 100° F., and the results of these tests after 22 days are given in the following table: The additives were employed in an amount of 0.05% by weight.

*Table 4*

| Additive | A. S. T. M. Photoelectric Color Index |
|---|---|
| None | 29 |
| A | 35 |
| B | 42 |
| F | 15 |
| E | 57 |

Here again, it will be noted that additive mixture E was considerably better than the individual components.

## EXAMPLE IV

This example shows the results of acid treating of the fuel oil before the incorporation of additives. A portion of the fuel oil was treated with 5 pounds of 98% sulfuric acid at room temperature. The results of the accelerated tests of different samples of the fuel oil, with and with-

out acid treatment, and with and without additives are shown in the following table:

*Table 5*

| Additive | A. S. T. M. Photoelectric Color Index | |
|---|---|---|
| | Untreated Fuel Oil | Acid Treated Fuel Oil |
| None | 0.5 | 14.7 |
| 0.05% Additive E | 2.2 | 79.9 |

It will be noted that with this particular fuel oil response to additive E was considerably improved by previous mild acid treatment.

EXAMPLE V

This example illustrates the benefits obtained by caustic treatment. The fuel oil used in this example was a West Texas virgin gas oil and was caustic washed prior to incorporation of the additive. The results of this test are shown in the following table. Prior to the accelerated tests, the fuel oil had a color index of 96.5.

*Table 6*

| Additive | A. S. T. M. Photoelectric Color Index |
|---|---|
| None | 77.4 |
| + 0.05% Additive E | 93 |

It will be noted that the sample fuel oil without additive dropped in color index from 96.5 to 77.4 and that use of the additive maintained the color at 93.

EXAMPLE VI

The fuel oil used in this example was a mixture of 50% virgin gas oil and 50% catalytic cycle stock. The blended fuel oil prior to storage, had a color index of 95. The following table shows the results of both the accelerated test and after storage at 100° F. for 22 days.

*Table 7*

| Additive | A. S. T. M. Photoelectric Color Index | |
|---|---|---|
| | Accelerated Test | Storage Test |
| None | 70.6 | 68 |
| 0.05% of Additive E | 83.8 | 80 |

It will be noted that additive mixture E served effectively to retard discoloration of the blend of virgin and cycle stocks. Further, this example illustrates the satisfactory correlation of the accelerated test with the actual storage test of 22 days.

We claim as our invention:

1. A fuel oil heavier than gasoline containing from about 0.0005% to about 1.0% by weight of an additive mixture comprising (1) from about 10% to about 50% by weight of a benzalaminoalkanol in which the alkanol group contains from about 2 to about 12 carbon atoms per molecule, (2) from about 10 to about 70% by weight of an alkanol amine containing from about 8 to about 40 carbon atoms per molecule, (3) from about 10 to about 70% by weight of an alkyl amine containing from about 6 to about 20 carbon atoms per molecule and (4) from about 1 to about 20% by weight of a metal deactivator comprising a compound capable of forming chelate compounds with metals.



2. The composition of claim 1 further characterized in that said additive mixture also contains a phenolic antioxidant in an amount of from about 10 to about 50% by weight of said mixture.

3. The composition of claim 1 further characterized in that said metal deactivator comprises disalicylal diamino propane.

4. A fuel oil heavier than gasoline containing from about 0.0005% to about 1.0% by weight of an additive mixture comprising (1) from about 10% to about 50% by weight of a benzalaminoalkanol in which the alkanol group contains from about 2 to about 12 carbon atoms per molecule, (2) from about 10 to about 70% by weight of an alkanol amine containing from about 8 to about 40 carbon atoms per molecule, (3) from about 10 to about 70% by weight of an alkyl amine containing from about 6 to about 20 carbon atoms per molecule, (4) from about 1 to about 20% by weight of a metal deactivator comprising a compound capable of forming chelate compounds with metals and (5) from about 10 to about 50% by weight of a solvent comprising isopropanol.

5. A fuel oil heavier than gasoline containing from about 0.0005% to about 0.1% by weight of an additive mixture comprising (1) from about 10% to about 50% by weight of benzalaminopropanol, (2) from about 10 to about 70% by weight of an alkanol amine containing from about 8 to about 40 carbon atoms per molecule, (3) from about 10 to about 70% by weight of an alkyl amine containing from about 8 to about 14 carbon atoms per molecule, (4) from about 1 to about 20% by weight of disalicylal diamino propane and (5) from about 10 to about 50% by weight of isopropanol.

6. The composition of claim 5 further characterized in that said additive mixture also contains a phenolic antioxidant in an amount of from about 10 to about 50% by weight of said mixture.

7. A fuel oil heavier than gasoline containing a stablizing amount of an additive mixture comprising (1) from about 10% to about 50% by weight of a benzalaminoalkanol in which the alkanol group contains from about 2 to about 12 carbon atoms per molecule, (2) from about 10 to about 70% by weight of an alkanol amine containing from about 8 to about 40 carbon atoms per molecule, (3) from about 10 to about 70% by weight of an alkyl amine containing from about 6 to about 20 carbon atoms per molecule and (4) from about 1 to about 20% by weight of a metal deactivator comprising a compound capable of forming chelate compounds with metals.

8. The composition of claim 7 further characterized in that said metal deactivator comprises disalicylal diamino propane.

9. A stabilizing composition suitable for preventing discoloration of fuel oils comprising (1) from about 10% to about 50% by weight of a benzalaminoalkanol in which the alkanol group contains from about 2 to about 12 carbon atoms per molecule, (2) from about 10 to about 70% by weight of an alkanol amine containing from about 8 to about 40 carbon atoms per molecule, (3) from about 10 to about 70% by weight of an

alkyl amine containing from about 6 to about 20 carbon atoms per molecule and (4) from about 1 to about 20% by weight of a metal deactivator comprising a compound capable of forming chelate compounds with metals.

10. The composition of claim 9 further characterized in that said metal deactivator comprises disalicylal diamino propane.

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**References Cited** in the file of this patent

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 1,989,528 | Rather et al. | Jan. 29, 1935 |
| 1,992,014 | Rogers et al. | Feb. 19, 1935 |
| 2,282,513 | Downing et al. | May 12, 1942 |
| 2,300,998 | White et al. | Nov. 3, 1942 |
| 2,346,663 | Chenicek | Apr. 18, 1944 |
| 2,361,339 | White et al. | Oct. 24, 1944 |