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## FUEL OIL COMPOSITION

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This invention relates to distillate fuel oil compositions containing pour point depressors.

In storage and use of heavy oils, such as lubricating oils, problems associated with pour point have long been in existence and have been recognized in the art. The pour point of an oil is defined as the lowest temperature at which the oil will pour or flow when chilled without disturbance under specified conditions. Recently, it has been discovered that pour point problems also exist in the storage and use of distillate fuel oils, particularly at low temperatures. Pour point problems arise through the formation of solid or semi-solid waxy particles within an oil composition. For example, in the storage of furnace oils or diesel oils during the winter months, temperatures may decrease to a point as low as  $-15$  to  $-25^{\circ}$  F. The decreased temperatures often cause crystallization and solidification of wax in the distillate fuel oil. This problem has been in part remedied by lowering the end point of oils used for blending furnace and diesel oils. It has also been suggested that the distillate fuel oils may be dewaxed such as by urea dewaxing. However, readjustment of end points causes loss of valuable product as blending material to distillate fuel oil stocks. Further, dewaxing operations are expensive.

Another approach in solving the problem has been to attempt to find a pour point depressor which will decrease the pour point of a distillate fuel oil. However, it has been found that the pour point depressors normally used for lubricating oils and other heavy oils are generally ineffective in lowering the pour point of a distillate fuel oil.

I have now discovered a pour point depressor which is useful in a fuel oil composition. The fuel oil composition of this invention comprises a distillate fuel oil and a small amount of the pour point depressor. The pour point depressor of this invention is a tertiary amine oxide having the following structural formula:



wherein at least one of the R's is an alkyl group containing from about one to about 22 carbon atoms or, more advantageously, from about 12 to about 20 carbon atoms. The other two R-groups may be the same or different aliphatic or aromatic hydrocarbon groups. The aliphatic groups are saturated or unsaturated and contain from about one to about 22 carbon atoms or, advantageously, from about 12 to about 20 carbon atoms. The aromatic hydrocarbon groups contain from about 6-10 carbon atoms. Combination groups of aliphatic and aromatic hydrocarbon substituents may also be used as the other two R-groups; such combination groups include aralkyl groups and alkaryl groups and contain from 7-30 carbon atoms. The preferred tertiary amine oxides are those wherein all of the R-groups are alkyl groups having from one to 22 carbon atoms and especially those having from 12 to 20 carbon atoms.

The tertiary amine oxides are used in the distillate fuel oil in amounts of from about 0.001 to about 5 weight percent and preferably from about 0.01 to about 0.05 weight percent. The tertiary amine oxides may also be prepared in concentrate form in a hydrocarbon or alcohol

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solvent such as benzene, toluene, xylene, isopropanol, methanol, and the like.

Where the tertiary amine oxide used has low solubility in the distillate fuel oil, solvents such as the above aromatic hydrocarbons and alcohols may be used in the distillate fuel oil in sufficient amounts to solubilize the tertiary amine oxide.

The tertiary amine oxides are prepared by oxidation of the corresponding tertiary amine using an oxidizing agent such as hydrogen peroxide, ozone, per acids, and the like. The reaction may be carried out in the presence of a polar organic solvent such as isopropanol, ethanol, acetic acid, butyrolactone, or the like. The reaction may take from two hours to 72 hours for substantial oxidation of the tertiary amine. The reaction time may be reduced by using a stronger oxidation agent as is known in the art. Where hydrogen peroxide is used as the oxidation agent, the oxidation reaction may conveniently be stopped when desired by adding platinum foil to the reaction mixture to deactivate the hydrogen peroxide; ferric chelate systems or enzyme systems may also conveniently be employed.

The tertiary amine which is oxidized to form the tertiary amine oxide for use in this invention, may be any tertiary amine corresponding to the above defined tertiary amine oxides. Examples of such tertiary amine oxides are as follows: di-methyl eicosyl amine oxide, di-isopropyl heptadecyl amine oxide, di-hexyl hexadecyl amine oxide, octyl di-heptadecyl amine oxide, ethyl di-octadecyl amine oxide, tri-dodecyl amine oxide, tri-lauryl amine oxide, tri-cresyl amine oxide, tri-capryl amine oxide, triononyl amine oxide, tri-isopropyl amine oxide, lauryl dibenzyl amine oxide, pentadecyl di-naphthyl amine oxide, di-hexyl ethylbenzyl amine oxide, stearyl di-(di-dodecylbenzyl) amine oxide, di-decyl di-ethyl-naphthyl amine oxide, butyl heptenyl phenyloctyl amine oxide, di-dodecyl naphthylbutyl amine oxide, di-methyl diphenyldodecyl amine oxide, di-isopropyl heneicosyl amine oxide, tri-dodecyl amine oxide, methyl di-hexylhexadecyl amine oxide, tri-docosyl amine oxide, di-hexenyl isodecyl amine oxide, isobutyl ethylhexyl kerylbenzyl amine oxide, etc., and homologues and isomers of the above. Additionally, commercial tertiary amines may be oxidized to form the tertiary amine oxides useful in this invention. Such commercial tertiary amines include those marketed under the trade name of "Armeen," such as Armeen M2HT (methyl di-hydrogenated tallow amine), Armeen DM16 (di-methyl hexadecyl amine), Armeen DM18D (di-methyl stearyl amine), Armeen DMCD (di-methyl coco amine), and Armeen DMSD (di-methyl soybean amine). Other tertiary amines which may be used are the Adogen 340 (tri-hydrogenated tallow amine) and Adogen 363 (tri-lauryl amine) and Alamine 336 (tri-capryl amine). In the nomenclature of commercial amines, terms such as "coco," "soybean," "tallow," and the like indicate the source of acid from which the group indicated thereby was derived. Each such group is usually a mixture of carbon chains differing slightly in length and/or configuration. However, these groups are well known in the additive art. The commercial amines are very useful and recommended because of their availability and relative low cost.

The distillate oil or distillate fuel oil is a hydrocarbon oil, such as for example, a diesel fuel, a jet fuel, a heavy industrial residual fuel (e.g., Bunker C), a furnace oil, a heater oil fraction, kerosene, a gas oil, or any other light oil. Of course, any mixtures of distillate oils are also intended. The distillate fuel oil may be virgin or cracked petroleum distillate fuel oil. The distillate fuel oil may advantageously boil in the range of from about 200 to

about 750° F., and preferably in the range of 350 to 650° F. The distillate fuel oil may contain or consist of cracked components, such as, for example, those derived from cycle oils or cycle oil cuts boiling heavier than gasoline, usually in the range of from about 450 to about 750° F. and may be derived by catalytic or thermal cracking. High-sulfur-containing and low-sulfur-containing oils such as diesel oils and the like may also be used. The distillate oil may, of course, contain other components such as addition agents used to perform particular functions, for example, rust inhibitors, corrosion inhibitors, anti-oxidants, sludge stabilizing compositions, etc.

The preferred distillate fuel oils have an initial boiling point in the range of from about 350 to about 475° F. and an end point in the range of from about 500 to about 650° F. The distillate fuel oil may advantageously have an A.P.I. gravity of about at least 30 and a flash point (Tag closed cup) not lower than about 110° F. and preferably above about 115° F.

The following are examples of the preparation of tertiary amine oxides suitable for use as distillate oil addition agents in accordance with this invention.

#### Examples

(1) As an example of the preparation of a tri-hydrogenated tallow amine oxide, 5 grams of Adogen 340 (Tri-hydrogenated tallow amine) was dissolved in 50 ml. of glacial acetic acid and 5 ml. of 30% hydrogen peroxide added in one portion. The resulting mixture was stirred for 48 hours. Platinum foil was then added to the reaction mixture to decompose excess hydrogen peroxide. Stirring was continued for about 68 hours, at which time a crust which had formed above the liquid phase was broken up. Stirring was continued for an additional 24 hours and the mixture was then filtered to isolate the product as a solid on the filter.

(2) As an example of the preparation of methyl di-hydrogenated tallow amine oxide, 5 grams of Armeen M2HT (methyl di-hydrogenated tallow amine) was dissolved in 50 ml. of isopropanol and 4 ml. of 30% hydrogen peroxide were added to the solution. The reaction mixture was stirred for 2 hours and allowed to stand for 48 hours. The reaction mixture was then filtered to remove 1.2 grams of unreacted starting material. The filtrate was taken to dryness under reduced pressure at room temperature to yield 6.0 grams of a white translucent syrup product containing some residual alcohol. The product was methyl di-hydrogenated tallow amine oxide.

(3) As an example of preparation of tri-lauryl amine oxide, 10 grams of Adogen 363 (tri-lauryl amine) were dissolved in 50 ml. of acetic acid and 7 ml. of 30% hydrogen peroxide were added to the resulting solution. The reaction mixture was stirred for 24 hours and platinum foil was added to decompose excess hydrogen peroxide. The mixture was then again stirred for 24 hours and acetic acid was evaporated under vacuum at room temperature. The resulting product was tri-lauryl amine oxide.

(4) Tri-capryl amine oxide was prepared as follows: 10 grams of tri-capryl amine (Alamine 336) were dissolved in 50 ml. of glacial acetic acid. Five ml. of 30% hydrogen peroxide were added to the solution. The resulting reaction mixture was stirred at room temperature (25° C.) for 72 hours. Platinum foil was then added and the mixture was stirred for an additional 24 hours. Acetic acid was removed by evaporation under a hood. The resulting product was tri-capryl amine oxide.

To illustrate this invention, a tertiary amine oxide was added to various distillate fuel oils and the effect of the tertiary amine oxide on the pour point of the fuel oil was measured. The following distillate fuel oils were used:

Fuel A—Desulfurized gas oil.

Fuel B—Light catalytic cycle oil (ASTM distillation: initial 420° F., and end point 621° F.)

Fuel C—Light catalytic cycle oil (ASTM distillation: initial 405° F., end point 638° F.)

Fuel D—A blend of 535 parts of light catalytic cycle oil and 215 parts of middle catalytic cycle oil.

Fuel E—A blend of equal parts light catalytic cycle oil (ASTM distillation: initial 404° F., end point 577° F.) and virgin diesel fuel oil.

Fuel F—A blend of 2 parts desulfurized gas oil and one part kerosene diesel oil.

Fuel G—A blend of 530 parts light catalytic cycle oil (ASTM distillation: initial 420° F., end point 621° F.) and 227 parts diesel oil.

Fuel H—A blend of 250 parts virgin gas oil, 280 parts heater oil, 167 parts middle catalytic cycle oil, and 60 parts light catalytic cycle oil.

Fuel J—A blend of 187 parts light catalytic cycle oil, 75 parts middle catalytic cycle oil, 338 parts virgin furnace oil, and 150 parts heater oil.

Fuel K—A blend of 150 parts light catalytic cycle oil, 75 parts middle catalytic cycle oil, 38 parts virgin furnace oil, and 487 parts heater oil.

The parts referred to in the above compositions of Fuels A through K are parts by volume.

To each distillate fuel composition listed above, the amounts of tri-hydrogenated tallow amine oxide indicated in the following table were added as a pour point depressor and the pour points were determined as recorded:

| Sample | Distillate Fuel Oil | Tri-hydrogenated tallow Amine Oxide, Wt. Percent | Pour Point, ° F. |
|--------|---------------------|--------------------------------------------------|------------------|
| 1      | A                   | 0                                                | -10              |
| 2      | A                   | 0.01                                             | -13              |
| 3      | A                   | 0.03                                             | -70              |
| 4      | A                   | 0.05                                             | -70              |
| 5      | A                   | 0.1                                              | -70              |
| 6      | B                   | 0                                                | -13              |
| 7      | B                   | 0.01                                             | -14              |
| 8      | B                   | 0.03                                             | -62              |
| 9      | B                   | 0.05                                             | -70              |
| 10     | B                   | 0.1                                              | -70              |
| 11     | C                   | 0                                                | +15              |
| 12     | C                   | 0.01                                             | +13              |
| 13     | C                   | 0.1                                              | -22              |
| 14     | D                   | 0                                                | -27              |
| 15     | D                   | 0.03                                             | -70              |
| 16     | E                   | 0                                                | -15              |
| 17     | E                   | 0.01                                             | -18              |
| 18     | E                   | 0.03                                             | -52              |
| 19     | E                   | 0.05                                             | -70              |
| 20     | E                   | 0.1                                              | -70              |
| 21     | F                   | 0                                                | -19              |
| 22     | F                   | 0.01                                             | -22              |
| 23     | F                   | 0.03                                             | -70              |
| 24     | G                   | 0                                                | -29              |
| 25     | G                   | 0.01                                             | -54              |
| 26     | G                   | 0.03                                             | -70              |
| 27     | H                   | 0                                                | -1               |
| 28     | H                   | 0.01                                             | -6               |
| 29     | H                   | 0.03                                             | -47              |
| 30     | H                   | 0.05                                             | -52              |
| 31     | H                   | 0.1                                              | -56              |
| 32     | J                   | 0                                                | -1               |
| 33     | J                   | 0.03                                             | -22              |
| 34     | J                   | 0.05                                             | -66              |
| 35     | J                   | 0.1                                              | -70              |
| 36     | K                   | 0                                                | -30              |
| 37     | K                   | 0.01                                             | -32              |
| 38     | K                   | 0.03                                             | -50              |
| 39     | K                   | 0.05                                             | -51              |
| 40     | K                   | 0.1                                              | -50              |

<sup>1</sup> Average of two runs.

The data presented in the above table demonstrate the remarkable ability of the addition agents of this invention in decreasing the pour point of distillate fuel oils.

It is evident from the data that the pour point depressors described herein are effective in very small concentrations, i.e., as little as 0.01 weight percent is often effective in noticeable lowering of pour point. It is also evident that often the pour point is depressed greatly using a concentration of 0.05 weight percent and, there-

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fore, the preferred range of use is from about 0.01 to about 0.05 weight percent although it may be advantageous, in many cases, to employ up to about 0.5 weight percent or more of the addition agent.

The methyl di-hydrogenated tallow amine oxide prepared in Example 2 above was added to a distillate fuel oil in the concentrations set out below with the resulting pour points as indicated:

| Additive concentration: | Pour point, ° F. |
|-------------------------|------------------|
| 0.00% -----             | 0 to -5          |
| 0.01% -----             | -4               |
| 0.10% -----             | -8               |
| 0.50% -----             | -46              |

The above data further illustrate the ability of the tertiary amine oxides as pour point depressors in small amounts, up to about 0.5 weight percent, in a distillate fuel oil.

Further, it has been discovered that distillate fuel oil compositions containing the tertiary amine oxides are stable under conditions of storage, i.e., do not lose their pour point depressing ability. As a demonstration of this advantage of the present compositions, 0.05 weight percent of tri-hydrogenated tallow amine oxide, the product of Example 1, were added to a distillate fuel oil. A blank distillate fuel oil was also prepared consisting of the same distillate fuel oil with no amine oxide additive. Both fuel oil compositions were stored for two months under increased temperature conditions (110° F.) to simulate storage of fuel oils under long periods of time. Throughout the test, the pour points of the distillate oils were determined as follows:

| Fuel Oil Compositions     | 0 Month<br>Pour<br>Point,<br>° F. | One<br>Month<br>Pour<br>Point,<br>° F. | Two<br>Months<br>Pour<br>Point,<br>° F. |
|---------------------------|-----------------------------------|----------------------------------------|-----------------------------------------|
| Blank -----               | -2                                | -2                                     | -2                                      |
| Containing Additive ----- | -46                               | -46                                    | -46                                     |

The tertiary amine oxides may, for convenience, be prepared as addition agent concentrates. Accordingly, the tertiary amine oxide is prepared in or dissolved in a suitable organic solvent therefor in amounts greater than 10% and preferably from about 25% to about 65%. The solvent in such concentrate may conveniently be present in amounts from about 35% to about 75%. The organic solvent preferably boils within the range of from about 100° F. to about 700° F. The preferred organic solvents are hydrocarbon solvents, for example, petroleum fractions such as naphtha, heater oil, mineral spirits and the like, because of their clean burning properties. The solvents selected should, of course, be selected with regard to possible beneficial or adverse effects it may have on the ultimate fuel oil composition. Thus, the solvent should preferably burn without leaving a residue and should be non-corrosive with regard to metal, and especially ferrous metals. Other desirable properties are obvious from the intended use of the solvent.

All percentages given herein are percentages by weight unless otherwise indicated.

It is evident from the foregoing that I have provided distillate fuel oil compositions containing tertiary amine oxides as pour point depressors effective in very small amounts.

I claim:

1. A fuel oil composition comprising a major amount

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of distillate fuel oil and a minor amount of a tertiary amine oxide having the structural formula:



wherein one R-group is an aliphatic hydrocarbon group having from one to about 22 carbon atoms and the remaining R-groups are selected from the class consisting of aromatic hydrocarbon groups having from 6 to about 10 carbon atoms, aliphatic hydrocarbon groups having from 1 to about 22 carbon atoms, aromatic hydrocarbon-substituted aliphatic hydrocarbon groups having from 7 to about 30 carbon atoms and aliphatic hydrocarbon-substituted aromatic hydrocarbon groups having from 7 to about 30 carbon atoms, said minor amount being sufficient to lower the fuel oil pour point.

2. The fuel oil composition of claim 1 wherein said distillate fuel oil is a mixture of virgin and cracked petroleum distillate fuel oils.

3. The fuel oil composition of claim 1 wherein said distillate fuel oil boils in the range of 350° to 650° F.

4. The fuel oil composition of claim 1 wherein said one R-group is an alkyl group having from about 12 to about 20 carbon atoms.

5. The fuel oil composition of claim 1 wherein said remaining R-groups are aliphatic hydrocarbon groups containing from one to about 22 carbon atoms.

6. The fuel oil composition of claim 2 wherein the cracked component is derived by cracking a cycle oil boiling heavier than gasoline.

7. The fuel oil composition of claim 4 wherein said remaining R-groups are alkyl groups having from about 12 to about 20 carbon atoms.

8. A fuel oil composition comprising a major amount of a petroleum distillate fuel oil and from about 0.01 to about 0.5 weight percent of a tri-alkyl amine oxide in which the alkyl groups contain from one to about 22 carbon atoms.

9. The fuel oil composition of claim 8 wherein said tri-alkyl amine oxide is tri-hydrogenated tallow amine oxide.

10. The fuel oil composition of claim 8 wherein said tri-alkyl amine oxide is methyl di-hydrogenated tallow amine oxide.

11. The fuel oil composition of claim 8 wherein said tri-alkyl amine oxide is tri-lauryl amine oxide.

12. The fuel oil composition of claim 8 wherein said tri-alkyl amine oxide is tri-capryl amine oxide.

13. A fuel oil composition comprising a major amount of a petroleum distillate fuel oil and from about 0.01 to about 0.05 weight percent of a tri-alkyl amine oxide having from about 12 to about 20 carbon atoms in each alkyl group.

14. A fuel oil composition concentrate containing from about 25% to about 65% of the tertiary amine oxide of claim 1 and from about 35% to about 75% of a hydrocarbon solvent boiling at a temperature in the range of from about 100° F. to about 700° F., said concentrate being capable of dilution with a distillate fuel oil to a tertiary amine oxide concentration in the range of from about 0.01 to about 0.05%.

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