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# TRANSESTERIFICATION PRODUCT

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The present invention is concerned with a multi-purpose additive and with its method of manufacture. The multi-purpose additive of the present invention functions to effectively reduce the pour point of base hydrocarbon compositions and also appreciably reduce the sediment. The multi-purpose additive of the present invention, in essence, comprises a copolymer of ethylene and vinyl acetate which is reacted with an amino acid and which is particularly potent in middle distillates. The ethlylene-vinyl acetate copolymer is subjected to transesterification of some of the acetate with amino acids which is promoted while distilling off acetic acid. This functions to introduce amine groups in the molecule and give the additive the power to inhibit sediment formation and also better the stability against color degradation.

With the increase in the use of hydrocarbon fuels of all kinds, serious problems have arisen in areas frequently subjected to low temperatures in the cold test characteristics of fuels. Particularly, serious problems have been encountered with heating oils and diesel and jet fuels that have too high a pour point, resulting either in distributional or operating difficulties or both. For example, the distribution of heating oils by pumping or syphoning is rendered difficult or impossible at temperatures around or below the pour point of the oil. Furthermore, the flow of the oil at such temperatures through the filters is not maintained, leading to equipment failures.

Also, the low temperature properties of petroleum distillate fuels boiling in the range between about 250° and about 750° F. have attracted increasing attention in recent years because of the growth of market for such fuels in subarctic areas and because of the development of turbo-jet aircraft capable of operating at altitudes where temperatures of —50° F. or lower are encountered.

It is therefore an object of the present invention to utilize an additive which is produced by the transesterification of a copolymer of ethylene and vinyl acetate with an amino acid. Also as heretofore mentioned, these multifunctional additives are particularly effective for middle distillates and lighter oils. In general, these oils boil in the range from about 250° F. to 750° F.

It is a still further object of the present invention to provide heating oils, diesel fuel oils, kerosenes and jet fuels having low pour points. Aviation turbo-jet fuels in which the polymers may be used normally boil between about 250° and about 550° F. and are used in both military and civilian aircraft. Such fuels are more fully defined by U.S. Military Specifications MIL–F–5624C, MIL–F–25554A, MIL–F–25558A, and amendments thereto. Kerosenes and heating oils will normally have boiling ranges between about 300° and about 750° F. and are more fully described in ASTM Specification D–396–48T and supplements thereto, where they are referred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the polymers may be employed are described in detail in ASTM Specification D–975–53T and later versions of the same specification.

The polymeric pour depressants and sediment inhibitors may, in accordance with the invention, be employed in conjunction with a variety of other additives commonly used in fuels such as those set forth above. Typical of such additives are rust inhibitors, anti-emulsifying agents, corrosion inhibitors, anti-oxidants, dispersants,



dyes, dye stabilizers, haze inhibitors, antistatic agents and the like. It will frequently be found convenient to prepare additive concentrates for use in the various types of fuels and thus add all of the additives simultaneously.

Other and further objects of the present invention will appear more clearly hereinafter.

The pour depressant and sediment inhibitor comprises an ethylene-vinyl acetate copolymer which is reacted with an amino acid. It is preferred that the parts by weight of ethylene in the copolymer be in the range from about 60–99% as compared to parts by weight of vinyl acetate in the range from about 40 to about 1%. A very desirable ethylene-vinyl acetate copolymer contains about 15 to 25% by weight of vinyl acetate, as for example, about 20% parts by weight of vinyl acetate.

The molecular weights of the ethylene-vinyl acetate copolymer are critical and should be in the range from about 1,000 to 3,000, preferably in the range from about 1,500 to 2,200. The molecular weights are determined by K. Rast's method (Ber., 55, 1051, 3727 (1922)). In general these copolymers are described in U.S. Patent 3,048,479 issued August 7, 1962, inventors Stephen Ilnyckyj and Charles B. Rupar and entitled, "Ethylene-Vinyl Ester Pour Depressant for Middle Distillates."

The ethylene-vinyl acetate copolymers as described which are reacted with an amino acid are used in a concentration in the range from about .001 to .5% by weight, preferably in a concentration in the range from about .005 to .1% by weight in the base hydrocarbon composition.

A very desirable method for the preparation of the copolymer is to conduct the polymerization reaction in a benzene solution using di-tertiary-butyl-peroxide as an initiator at a temperature in the range from about 280° to 340° F. The preferred temperature is about 300° F. The pressure is in the range from about 700 to 2,000 pounds, preferably at about 800 pounds. The autoclave or similar equipment containing the solvent, initiator and vinyl acetate is purged about three times with nitrogen, twice with ethylene and then charged with a sufficient amount of ethylene to yield the desired pressure when heated to the reaction temperature. During the polymerization, additional ethylene is added whenever the pressure drops by about 100 p.s.i.g. Polymerization is considered complete when it is less than 50 p.s.i.g. pressure drop per hour. The product is stripped free of solid and unreacted vinyl acetate under vacuum.

One method for the glycination of the copolymer is as follows:

Forty parts by weight of ethylene-vinyl acetate copolymer (50% in kerosene) was heated with 3.2 parts by weight of glycine to a temperature of about 110° C. The glycine gradually dissolved as the mixture was heated. A trace of p-toluene-sulfonic acid was added and a small amount of acidic distillate (3 ml.) was recovered from the reaction mixture during a 2 hour heating period. The reaction mixture was cooled at 25° C. and the unreacted glycine (1.7 parts by weight) precipitated from the product mixture. The product mixture was then taken up in heptane, washed with water, dried over magnesium sulfate and filtered. After removal of the heptane, the product showed strong N–H adsorption in the infrared spectrum at 3300° and 1600 $cm.^{-1}$ in addition to an acetate peak at 1750 $cm.^{-1}$. While a temperature of about 110° C. is preferred, the temperature of the glycination reaction may be in the range from about 90° C. to 130° C., preferably in the range from about 105° C to 115°C.

Other amine acids which may be used are, for example, alanine acid, serine acid, phenyl alanine acid, tyrosine acid and 11-amino-undecanoic acid. These acids and their corresponding lactams may also be used.

Although a copolymer of ethylene and vinyl acetate is preferred, other copolymers of ethylene with vinyl esters may be used such as vinyl propionate, vinyl butyrate and vinyl stearate. It is preferred that the vinyl ester have from about 4 to 7 carbon atoms.

The transesterification reaction may be conducted so as to substitute amine acid groups up to 100% for the acetate groups. It is preferred that from about 20 to 50% of the acetate groups be replaced, preferably about 25 to 35% of the acetate groups be replaced, as for example from about 30 to 31%.

As pointed out, these multi-purpose additives are added to middle distillate fuels. A typical distillate fuel boiling in the range from 250° to 750° F. to which the present additives may be added is a middle distillate heating oil. Fuels of this type are of commercial grade and have typical properties as follows:

TABLE I

| | |
|---|---|
| Compositions: | |
| Straight run gas oil, vol. percent | 50 |
| Cat. cracked gas oil, vol. percent | 50 |
| Inspections: | |
| Gravity, ° API | 28.7 |
| ASTM pour, ° F., no additive | +20 |
| Viscosity, centistokes at 100° F. | 3.60 |
| Distillation ASTM, ° F.: | |
| I.B.P. | 308 |
| 10% | 466 |
| 50% | 560 |
| 90% | 628 |
| F.B.P. | 670 |

In order to further illustrate the invention, the specific composition given above was tested using a base fuel having the following characteristics.

TABLE II

| | |
|---|---|
| Composition: | |
| Straight run gas oil, percent | 80 |
| Cat. cracked gas oil, percent | 20 |
| Aniline point, ° F. | 140 |
| Gravity specific at 78° F. | 0.8426 |
| ASTM pour ° F. no additive | 0° C. |
| ASTM cloud point | +2° F. |

The results of these tests are illustrated in the following table.

TABLE III

| Test No. | Oil Blend | Hrs. Test (at 265° F.) | Sediment* (mg./100 ml.) |
|---|---|---|---|
| I | Uninhibited No. 2 Heating Oil | 6 | 1 7 |
| II | Heating Oil plus 0.007% Copolymer of ethylene and vinyl acetate. | 6 | 1.8 |
| III | Heating Oil plus glycinated Copolymer of II (0.02%). | 6 | 0.34 |

* The accelerated stability test consists of heating a sample to a fixed temperature, while blowing air through the sample, for a specified length of time; then cooling it, filtering (0.5μ pore size filter) and weighing any sediment formed; and measuring the amount of white light transmitted through the filtrate, relative to distilled water (100% light transmission).

From the above it is apparent that the glycinated copolymer was extremely effective in that the sediment was reduced from 1.7 to 0.34.

Additional tests were conducted to determine the potency of the additive with respect to lowering the pour point. The results of these tests are shown in the following table.



TABLE IV

| Heating Oil Tested | Original Pour-pt., ° F. | Lowering of pour-point, degrees F, upon addition of 0.06% | |
|---|---|---|---|
| | | Untreated Copolymer | Glycinated Copolymer |
| A | −5 | 35 | 35 |
| B | +20 | 55 | 65 |
| C | 0 | 25 | 25 |

The above data shows that the glycinated copolymer is as potent as the original untreaded copolymer for lowering the pour point of middle distillates.

Thus the present invention is concerned with a multi-purpose middle distillate additive which comprises a copolymer of ethylene and a vinyl fatty acid ester which has been transesterified with an amine acid. The additive is very effective for reducing the pour point, for reducing sediment and for imparting color stability to the middle distillate.

What is claimed is:

1. A hydrocarbon composition of improved pour and improved stability comprising a hydrocarbon oil boiling in the range from about 250 to 750° F. and an effective amount of an additive which is a transesterification reaction product between a copolymer of ethylene and a vinyl fatty acid ester, having a molecular weight of from 1,000–3,000 with a hydrocarbon amino acid.

2. Composition as defined by claim 1 wherein said amino acid is glycine.

3. Composition as defined by claim 2 wherein said vinyl acid ester is vinyl acetate.

4. Composition as defined by claim 1 wherein said reaction product is one wherein about 20 to 50% of the acetate groups of the copolymer are replaced with amino acid groups.

5. Compositions as defined by claim 4 wherein about 25 to 35% of the acetate groups are replaced with amino acid groups.

6. Composition as defined by claim 1 wherein the amount of reaction product present is in the range from about .001 to .5% by weight.

7. Composition as defined by claim 6 wherein the amount of reaction product present is in the range from about .005 to 0.1% by weight.


**References Cited by the Examiner**

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