MIDDLE DISTILLATE POURED POINT DEPRESSANTS


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6 Claims. (Cl. 44—62)

The present invention relates to improving the flow at low temperatures and at poured point characteristics of middle distillates. More particularly, the invention relates to the preparation of improved low cold test hydrocarbon fuels, in particular heating oils and diesel fuels, aviation, and other fuels that are subject to low temperatures. In accordance with the present invention, an improved class of pour depressants are utilized in conjunction with surface active agents in middle distillates. The preferred class of pour depressants are alkylated polystyrene compounds and copolymers of ethylene and vinyl acetate which copolymers have a molecular weight between 700 and 5,000. Preferred surface active agents for utilization in combination with these pour depressants comprise sulfonic acid and various salts of sulfonic acid. The preferred salts are those of Group II metals of the periodic table, particularly the alkaline earth metals and zinc. Very desirable metals are calcium and barium, particularly the calcium sulfonates.

With the increase in the use of hydrocarbon fuels of all kinds, a serious problem has arisen in areas frequently subject to low temperatures in the cold test characteristics of fuels. Particularly, serious problems have been encountered by heating oils and diesel 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 cannot be maintained, leading to the failure of the equipment to operate.

It is, of course, well known to add pour depressants to lubricating oils to lower the pour point. These lube oil additives, mostly high molecular weight organic compositions formed by alkylation of benzene or naphthlene or derivatives thereof or by polymerization of lower molecular weight methacrylates, or by condensation polymerization of various kinds, are not satisfactory in service with middle distillate and lighter fuels. Poor performance of these additives might possibly result from the structural differences between waxes occurring in lubricating oils and so-called middle distillates.

A wide variety of compounds have been found to be effective as pour point depressants for lubricating oil. Among the best known are “Paraflo”, “Santoport” and “Acryloid” and their modifications. They are prepared either by condensing aromatic compounds with long chain paraffins, such as wax, or by condensing olefinic esters. It is generally considered that these pour depressants are effective in that in cooling an additive-containing oil, the hydrocarbon chain of the additive becomes incorporated into the crystal lattice of the separated wax, while the other part of the pour depressant molecule prevents the crystals from adhering together to form a gel structure. The failure of these additives to be effective in middle distillates may at least in part be due to the basic difference in the composition between the wax in lubricating oils and that in middle distillate fuels.

It is, therefore, the principal object of the present invention to set forth an improved pour depressant for middle distillate and lighter fuels. The boiling ranges of these oils are generally about 250° to 750° F. The petroleum distillate fuels in which the additive materials of the invention are employed consist of a major proportion, at least 95%, of liquid hydrocarbons boiling at temperatures between about 70° F. and about 750° F. These fuels include gasolines such as aviation, marine and automotive or motor gasolines, aviation fuels such as JP-1, JP-4, and JP-5 fuels, and diesel fuels such as marine, stationary and automotive diesel engine fuels. Aviation fuel consists of at least 95% of a mixture of volatile hydrocarbons. It is defined by U.S. Military Specifications MIL-F-5616 and MIL-F-5624 C. Its volatility is such that its end point does not exceed 572° F. Its viscosity is between 0.5 and 1.5 centistokes at 100° F.

Diesel fuels as referred to in connection with the invention consist of at least 95% of a mixture of hydrocarbons boiling between 250° F. and 750° F., either by ASTM Method D 86—56 when their end points do not exceed 600° F. or by ASTM Method D 158—54. Diesel fuels are defined by ASTM Specification D 975—53T and fall into Grades 1D, 2D and 4D, in all of which the additive materials of the invention may be used. They have viscosities between 1.4 and 26.4 centistokes.

The liquid fuels in which the additive materials may be incorporated thus comprise at least 95% by weight of a mixture of hydrocarbons having a boiling range between the limits of 75° F. and 750° F. and a viscosity between the limits of 0.264 and 26.4 centistokes at 100° F.

As pointed out heretofore, one class of pour depressants to be used in conjunction with the sulfonic salts are certain alkylated polystyrene compounds. These alkylated polystyrene compounds are prepared with certain olefins and have a critical composition. The olefin should have a molecular weight in the range 200 to 250 and if it is a mixture at least 95 mole percent of the olefins should have molecular weights individually in the range of 170 to 280. The alkylates of interest have the following structure:

\[
\text{H}\left(\text{CH} = \text{CH_2}\right)_{x}\text{H} \quad \text{or} \quad \text{H}\left(\text{CH} = \text{CH_2}\right)_{y}\text{H}
\]

\[
\left(\text{R}_1 = \text{C} = \text{R}_2\right)\quad \text{or} \quad \left(\text{R}_1 = \text{C} = \text{R}_2\right)
\]

\[
\text{R}_1 \text{ is an alkyl group, straight or branched, containing 9 carbon atoms or less while R}_2 \text{ is a straight-chain alkyl group containing 10 carbon atoms or more, x is the number from 3 to 15 inclusive and y is 0.75 to 2.00.}
\]

All products were made under the reaction conditions of solvent, temperature, catalyst and finishing procedure as described in U.S. Patent No. 2,756,265 assigned to Esso Research and Engineering Company, entitled “Alkylated Polystyrene Pour Depressants,” Inventor: William C. Hollyday, Jr.
Broadly, the process comprises the steps of dissolving the desired polystyrene in an inert solvent and heating the mixture until the polystyrene is completely in solution. The mixture is cooled to the desired reaction temperature at which time the nitrobenzene and the Friedel-Crafts catalyst is added. The alkylating agent is added dropwise and the reaction temperature selected is maintained by cooling or heating as necessary. After the completion of the reaction, the alkylation is purified by well known techniques, among which is precipitation with methanol, dissolving in hexane and reprcipitating several times with methanol or isopropanol. If desired, the alkylated material may be dissolved in oil, washed with alkaline solutions, and the oil solution then steam stripped to result in the final product.

For obtaining the superior pour point depressants of this invention, it is desired that the polystyrene starting material have an intrincic viscosity within a range of about 0.2 to 2.0, preferably 0.8 to 1.5. These viscosities correspond to molecular weights within a range of from 10,000 to 75,000 preferably 30,000 to 60,000 Staudinger, if the constant for isobutylene polymers is assumed to apply. Since the amounts of the other reactants are based on the weight of the polystyrene, the amount of polystyrene used will depend upon restrictions such as equipment capacity, etc. The cryoscopic molecular weight after alkylation was about 700 to 3,000; the intrinsic viscosities of about 0.4 to 0.4. The 700 molecular weight composites, in essence, a trimer containing three alkylated phenyl groups, whereas the 3,000 molecular weight composites, in essence, about eight alkylated phenyl groups.

The alkylating agent chosen for the preparation of the improved pour point depressants of this invention will be olefinic in nature and will preferably contain from 14 to 18 carbon atoms in a straight chain. Although dodecene-1 through eicosene and cracked wax are used in the examples specifically detailing the instant invention, any olefinic material having the above requirements may be used. It is preferred that equimolar quantities of polystyrene and the alkylating agent be used, however, from 0.8 to 2.0 mols of alkylating agent per mol equivalent of polystyrene is operable.

These alkylated polystyrenes should be prepared wherein the olefin mixture has a molecular weight of about 224 (that of n-hexadecene). The polystyrenes should have a molecular weight within a range of from about 10,000 to 75,000, preferably 30,000 to 60,000 Staudinger. These molecular weights correspond to intrinsic viscosities within the range of from 0.2 to 2.0, preferably 0.8 to 1.5. The alkylating agent contemplated contains 12 to 20 carbon atoms in a straight chain. A chlorinated aromatic hydrocarbon is used as a solvent and a Friedel-Crafts catalyst in amounts varying between 10 and 20% by weight based on the weight of the polystyrene. The preferred catalyst modifier, nitrobenzene, is present in amounts so that the mol ratio of nitrobenzene to the catalyst is from 0.2 to 0.8. Reaction temperatures within a range of from 80° to 150° C. are used. These operable reaction conditions are so adjusted that in the relationship:

\[ K = \left(\frac{\alpha}{T}\right)^{\beta} \]

K varies between 6.0 and 15, where C equals the weight ratio of catalyst to polystyrene, T is the temperature ° F., and R is the ratio of mols of catalyst modifier to mols of aluminum chloride. By this particular process advantageous yields of an alkylated polystyrene pour depressant having an overall activity in a wide range of lubricating oils may be obtained.

As pointed out heretofore, the pour depressant agents have a cryoscopic molecular weight in the range from about 700 to 3,000 and an intrinsic viscosity in the range from about 0.1 to 0.5. These compounds are used in a weight concentration of about 0.002 to 2.0% of the weight of the product. About 0.005 to 0.25 weight percent. A very desirable concentration of to be used is in the range from about 0.025 to 0.1 weight percent.

Another group of pour depressants to be used in conjunction with the sulfonic acid salts comprise an ethylene-vinyl acetate copolymer. It is preferred that the parts by weight of ethylene in the copolymer be in the range from about 60 to 90% 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 40% by weight of vinyl acetate, 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 5,000, preferably in the range from about 1,500 to 4,000. The molecular weights are determined by K. Rast's method (Ber. 55, 1085, 3727 (1922)). The intrinsic viscosities fall in the range from 0.08 to 0.50.

The ethylene-vinyl acetate copolymer as described above is used in a concentration in the range from about 0.001 to 5% by weight, preferably, in a concentration in the range from about 0.05 to 2% by weight. The low molecular weight copolymers may be prepared by any peroxide process. In some instances, it may be desirable to first prepare a higher average molecular weight polymerization product and recover from that product material having a molecular weight within the range between about 1,000 and about 3,000. Since such polymerization products normally consist of a smear of polymers whose molecular weights vary over a wide range, an effective method for recovering the 1,000 to 3,000 molecular weight portion therefrom is to extract the product with a solvent such as normal heptane or methyl-ethyl ketone.

Other methods for obtaining the low molecular weight materials include thermal degradation of the high molecular weight polymer or treatment of the high molecular weight polymer with ozone in order to break the polymer chains. Still other methods also useful will be apparent to those skilled in the art.

A very desirable method is to conduct polymerization in a benzene solution using di-tert.-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 500 pounds. The autoclave or similar equipment containing the solvent, initiator and vinyl acetate is purged about 4 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 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.

The sulfonic acid and sulfonic acid salts which comprise the surface active agents of the present invention to be used in conjunction with the hereinbefore described pour depressants are prepared as follows:

The sulfonic acid from which the sulfonates were derived was prepared during the manufacture of a white oil from a lubricant base stock. The lubricant base stock had a viscosity of about 3.22 cs. at 210° F. and 14.4 cs. at 100° F. and an API gravity of 29.6, and was treated with a mixture of sulfuric acid and sulfur trioxide (80/20 by weight). During the sulfonation the temperature was kept between about 120 and 140° F. with cooling. The sulfonic acid was extracted from the unsulfonated hydrocarbon with a water and isopropyl alcohol mixture. The free sulfonic acid was isolated by evaporating the isopropyl alcohol and water.

The sulfonic acid had a molecular weight of about 525 and an average composition corresponding to the formula C_8H_8(C_3H_3S) SO_3H. The actual composition of this and other sulfonates derived from petroleum base stocks is
Quite complicated. The sulfonic acid is actually a mixture of materials containing naphthenic (saturated) as well as aromatic rings and various alkyl groups. Different molecules may also contain more than one ring (which may or may not be condensed), and more than one alkyl group.

Various metal salts of the sulfonic acid were prepared by neutralizing the acid with hydroxides of metals. The sulfonic acid dissolved in kerosene readily took up the hydroxides from aqueous solutions or suspensions to give a solution of the metal sulfonate in kerosene.

Sodium, calcium, aluminum, and stannic sulfonates among others were prepared in this way.

Various amounts of the pour depressants and the various sulfonates in kerosene were blended into distillate fuels and tested for pour depressant activity. A typical distillate fuel boiling in the range from 230° to 750° F, to which the present additives may be added are middle distillate heating oils. These fuels are of commercial grade and have typical properties as follows:

**Composition:**
- Straight run gas oil: 40
- Cat. cracked gas oil: 60

**Inspections:**
- Gravity, *API: 29.1
- ASTM pour, °F, no additive: 25
- Flash Pensky-Martin, °F: 192
- Distillation ASTM, °F—
  - 1°F: 398
  - 10°F: 492
  - 50°F: 566
  - 90°F: 612
  - F.B.P.: 644

The improvements obtained by adding the additives in accordance with the present invention are set forth in the following table. All pour points quoted hereafter were obtained by ASTM Method D-97-47.

In a first series of tests, an alkylated polystyrene was as described and having an intrinsic viscosity of 0.122 and a molecular weight of about 925 was added to a cracked heating oil stock from a Venezuelan crude which had a 25°F pour point. The inspections of this cracked heating oil were as follows: boiling range 408-660°F, API gravity 23.7, viscosity 3.62 cs. at 100°F.

The tests used in the first series of tests comprised the calcium salts, the sodium salts, the aluminum salts, the stannic salts, and the acid itself. The results of these tests are shown in the following Table I wherein alkyl PS represents alkylated polystyrene.

From the foregoing, it is apparent that calcium sulfonate has an appreciable effect in enhancing the pour depressant activity, in cracked stocks, of both the alkylated aromatic (Table I) and the ethylene-vinyl acetate copolymer (Table II). Its effect when utilized in straight run stocks is somewhat lessened (Table III).

### Table I

**EFFECT OF SURFACE ACTIVE AGENTS ON THE POUR DEPRESSANT ACTIVITY OF ALKYLATED POLYSTYRENE**

<table>
<thead>
<tr>
<th>Alkyl polystyrene blends</th>
<th>Calcium sulfonate blends</th>
<th>Combination blends—Pour point, °F, blends with alkyl PS plus sulfonate</th>
<th>Weight percent alkyl PS</th>
<th>Weight percent calcium sulfonate</th>
<th>Pour point, °F</th>
<th>Pour point, °F</th>
<th>Pour point, °F</th>
<th>Pour point, °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.01</td>
<td>0.01, +15</td>
<td>0.01</td>
<td>0.01, +15</td>
<td>0.01, +15</td>
<td>0.01, +15</td>
<td>0.01, +15</td>
<td>0.01, +15</td>
</tr>
<tr>
<td>0.03</td>
<td>0.03</td>
<td>0.03, +15</td>
<td>0.03</td>
<td>0.03, +15</td>
<td>0.03, +15</td>
<td>0.03, +15</td>
<td>0.03, +15</td>
<td>0.03, +15</td>
</tr>
<tr>
<td>0.05</td>
<td>0.05</td>
<td>0.05, +15</td>
<td>0.05</td>
<td>0.05, +15</td>
<td>0.05, +15</td>
<td>0.05, +15</td>
<td>0.05, +15</td>
<td>0.05, +15</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.10, +15</td>
<td>0.10</td>
<td>0.10, +15</td>
<td>0.10, +15</td>
<td>0.10, +15</td>
<td>0.10, +15</td>
<td>0.10, +15</td>
</tr>
</tbody>
</table>

1 In a cracked heating oil stock from Venezuela crude, +25°F original pour point.

### Table II

**EFFECT OF SURFACE ACTIVE AGENTS ON THE POUR DEPRESSANT ACTIVITY OF ETHYLENE/VINYL ACETATE COPOLYMER**

<table>
<thead>
<tr>
<th>Copolymer blends</th>
<th>Calcium sulfonate blends</th>
<th>Combination blends—Pour point, °F, blends with copolymer plus sulfonate</th>
<th>Weight percent copolymer</th>
<th>Weight percent calcium sulfonate</th>
<th>Pour point, °F</th>
<th>Pour point, °F</th>
<th>Pour point, °F</th>
<th>Pour point, °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.01</td>
<td>0.01, +15</td>
<td>0.01</td>
<td>0.01, +15</td>
<td>0.01, +15</td>
<td>0.01, +15</td>
<td>0.01, +15</td>
<td>0.01, +15</td>
</tr>
<tr>
<td>0.02</td>
<td>0.02</td>
<td>0.02, +15</td>
<td>0.02</td>
<td>0.02, +15</td>
<td>0.02, +15</td>
<td>0.02, +15</td>
<td>0.02, +15</td>
<td>0.02, +15</td>
</tr>
<tr>
<td>0.05</td>
<td>0.05</td>
<td>0.05, +15</td>
<td>0.05</td>
<td>0.05, +15</td>
<td>0.05, +15</td>
<td>0.05, +15</td>
<td>0.05, +15</td>
<td>0.05, +15</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.10, +15</td>
<td>0.10</td>
<td>0.10, +15</td>
<td>0.10, +15</td>
<td>0.10, +15</td>
<td>0.10, +15</td>
<td>0.10, +15</td>
</tr>
</tbody>
</table>

1 In a cracked heating oil stock from Venezuela crude, +25°F original pour point.

### Table III

**EFFECT OF SURFACE ACTIVE AGENT ON POUR DEPRESSANT ACTIVITY**

<table>
<thead>
<tr>
<th>Four depressant</th>
<th>Weight percent polymer</th>
<th>Four point, °F, with additive indicated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylated polystyrene</td>
<td>0.01</td>
<td>-20</td>
</tr>
<tr>
<td>Ethylene/vinyl acetate copolymer</td>
<td>0.02</td>
<td>-20</td>
</tr>
</tbody>
</table>

1 In a straight run heating oil stock from Venezuela crude, +25°F original pour point.

2 Calcium sulfonate added equal to polymer.
In a fourth series of tests, calcium sulfonate was used in conjunction with both classes of polymers wherein the base stock was a mixed straight run and cracked stock from a Venezuelan crude. This stock had a boiling range of 408–660° F., an API gravity of 33.0 and a viscosity of 3.70 cs. at 100° F.

The results of these tests are shown in the following Table IV.

### Table IV

<table>
<thead>
<tr>
<th>Polymer plus calcium sulfonate 1</th>
<th>Weight percent polymer 2</th>
<th>Polymer only 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylated polystyrene 4</td>
<td>0.01</td>
<td>+10</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0</td>
</tr>
<tr>
<td>Ethylene/vinyl acetate copolymer</td>
<td>0.01</td>
<td>+5</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>+5</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>+5</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>+5</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>+5</td>
</tr>
</tbody>
</table>

1 In a mixed straight run/cracked (80/20) heating oil stock from Venezuelan crude, +10° F. original pour point.
2 Constant amount (0.05 weight percent) calcium sulfonate in each blend.

From the above, it is apparent that in mixed cracked/straight run stocks, calcium sulfonate has a desirable effect on the copolymer and a lesser effect on the alkylated aromatic.

In a fifth series of tests, a mixed heating oil from a Canadian crude was used utilizing the various surface active agents. The base stock had a boiling range of 316 to 685° F. and an API gravity of 28.3.

The results of these tests are shown in the following Table V.

### Table V

<table>
<thead>
<tr>
<th>Polymer plus calcium sulfonate 1</th>
<th>Weight percent polymer 2</th>
<th>Polymer only 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylated polystyrene 4</td>
<td>0.01</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0</td>
</tr>
<tr>
<td>Ethylene/vinyl acetate copolymer</td>
<td>0.01</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0</td>
</tr>
</tbody>
</table>

1 In a mixed straight run/cracked heating oil stock from Canadian crude, +20° F. original pour point.
2 Colloidal barium carbonate dispersed in calcium sulfonate solution.
3 Product from treatment of 780 molecular weight polybutene with weight percent 3P2S6, then neutralized with high alkalinity calcium sulfonate.

In a sixth series of tests, a 50/50 mixture of an alkylated polystyrene was used in conjunction with a copolymer of ethylene/vinyl acetate in various base stocks. The cracked stock had a boiling range of 408–660° F., an API gravity of 23.7, and a viscosity of 3.62 cs. at 100° F. The straight run stock had a boiling range of 354–624° F., an API gravity of 37.6, and a viscosity of 2.35 cs. at 100° F. The mixed stock had a boiling range of 408–660° F., an API gravity of 33.0 and a viscosity of 3.70 cs. at 100° F.

The results of these tests are shown in the following Table VI.
3. The composition as defined by claim 1 wherein said petroleum sulfonic acid salts are salts of metals of Group II of the periodic table.

4. The composition as defined by claim 1 wherein said petroleum sulfonic acid salts are alkaline earth metals.

5. The composition as defined by claim 1 wherein said petroleum sulfonic acid salt is zinc sulfonate.

6. The composition as defined by claim 1 wherein said petroleum sulfonic acid salt is calcium sulfonate.

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