ABSTRACT OF THE DISCLOSURE

Hydrocarbon oil which loses fluidity at low temperature containing, in a pour point depressant concentration, a copolymer of aryl-C_{10}-C_{20} alkylene and unsaturated ester. Specific pour point depressants are copolymer of styrene-methylethacrylate or copolymer of styrene-vinyl acetate.

BACKGROUND OF THE INVENTION

The problems associated with the loss of fluidity of hydrocarbon oils at low temperatures are of considerable concern. Such loss of fluidity interferes with the satisfactory storing and transporting of the oil, as well as in mixing or blending of different oil fractions and in filtering operations. This problem is of increasing concern with the discovery of oil in subarctic areas, with the use of jet fuels at altitudes where temperatures of —50° F. or lower may be encountered, etc.

Such hydrocarbon oils are sometimes referred to as heavier oils and contain components which, upon encountering low temperatures, crystallize to form solid precipitates. These crystals become active centers for further crystallization, with the result that the oil congeals and loses its free flowing properties. The oils are of diversified chemical composition and many of the heavier oils contain waxy components in varying concentrations. These waxy components crystallize readily at low temperatures. Because of the variations in chemical compositions, different oils respond differently to pour point depressant additives. Accordingly, there is a need for novel pour point depressants which will serve to improve the flowing properties of the oils at low temperatures.

DESCRIPTION OF THE INVENTION

The present invention is directed to the use of particular copolymers as pour point depressants in such oils. The oils may be classified as those having pour points of above about —10° F. The oil may have an initial boiling point as low as 175° F. and end boiling point of 1000° F. or more but, as hereinbefore set forth, contains components which are responsible for the loss of fluidity. Illustrative examples of such oils include middle distillates, specialty oils, lubricating oils, residual oils, crude oils, etc. These oils may be untreated or resulting from conventional fractionation, solvent extraction, caustic treating, acid treating, dewaxing, thermal cracking, catalytic cracking, reforming or other processing operations, etc. The middle distillates include oils within the boiling range of from about 250° to 750° F. and include kerosene, jet fuel, diesel oil, burned oil, gas oil, fuel oil, light cycle oil, specialty oils such as solvent oils, cleaning oils for use in cleaning metallic equipment, electrical insulating oil which is used in transformers or circuit breakers, hydraulic oils, etc. The lubricating oils may be conventional lubricating oils having boiling points, for example, within the range of 650° to 1050° F. or more or selected fractions thereof for special uses. The residual oils may result from fractionation to remove lower boiling components or heavier oils resulting from processing operations and may have initial boiling points of 600° F. or more. As mentioned earlier, problems are encountered in the transportation and storage of crude oils and reduced crude oils at low temperatures and especially in cold climates.

In one embodiment, the present invention relates to a hydrocarbon oil containing components which cause the oil to lose fluidity at low temperature, said oil containing, in a pour point depressant concentration, a copolymer of aryl-C_{10}-C_{20} alkylene and unsaturated ester of the formula:

\[
\begin{align*}
\text{H}_2\text{C}-\text{C}=\text{O}-\text{R'} & \quad \text{or} \\
\text{H}-\text{C}=\text{C}-\text{O}-\text{R'}
\end{align*}
\]

in which \( R \) is hydrogen or \( C_1-C_6 \) alkyl and \( R' \) is \( C_1-C_2 \) alkyl.

The copolymer composition also may contain all or a portion of the free radical initiator used in the preparation of the copolymer, as well as some of the solvent, when employed, which is not subsequently removed from the composition. However, the initiator will be in a minor concentration and the solvent probably is present in a chemically uncombined state. Such retained solvent will increase solubility of the copolymer and, as will be hereinafter set forth, the copolymer may be commingled with additional solvents to form a concentrate for use as a pour point depressant.

As hereinbefore set forth, one component of the copolymer is an aryl-C_{10}-C_{20} alkylene and preferably a phenyl-C_{5}-C_{8} alkylene which also may be named as an alkynyl aromatic. In a particularly preferred embodiment, the double bond of the alkynyl moiety is positioned between the alpha and beta carbon atoms and is in close proximity to the aromatic ring. In this embodiment, styrene is an especially preferred alkynyl aromatic. Other preferred alkynyl aromatics contain up to 6 carbon atoms in the alkynyl moiety and include alpha-methylstyrene, alpha-ethylstyrene, alpha-propylstyrene, and alpha-butyln styrene. In a preferred embodiment, the copolymer, but not necessarily with equivalent results, the alkynyl moiety may contain from 6 to 22 carbon atoms and may contain 2 or more double bonds therein, with a double bond in a terminal position and a terminal carbon atom to which are attached two hydrogen atoms. Such higher boiling olefinic materials may be separated as specific fractions from particular processing steps. The phenyl alkynyl may be prepared by conventional alkylation of benzene with the olefin or in any other suitable manner. In still another embodiment instead of the phenyl alkynyl, other vinyl aromatics may be used as vinyl naphthalene, alpha-methylvinyl naphthalene, etc., but not necessarily with equivalent results.

In another embodiment, the aryl alkynyl may contain one or more substituents attached to the aryl ring. These substituents may be selected from alkyl of 1 to 12 carbon atoms, alkoxly containing from 1 to 12 carbon atoms in the alkynyl moiety, phenoxy, hydroxy, carboxyl, alkylamino, amino, halogen and preferably chlorine or bromine, etc. In a preferred embodiment, only one such substituent is attached to the phenyl ring and preferably in a position para to the alkynyl moiety. When two substituents are attached to the phenyl ring, they preferably are in the 3,4- or 3,5-positions.

Another component of the copolymer is an unsaturated ester of the formula hereinbefore set forth. The formula I, to the left illustrates esters which may be genetically termed as vinylalkanoates and illustrative examples include vinyl acetate, vinyl propionate, vinyl butyrate, preferably vinyl isobutyrate, vinyl valerate, vinyl hexanoate, vinyl heptanoate, vinyl caprylate, vinyl nonanoate, vinyl decanoate, vinyl laurate, vinyl myristate, vinyl palmitate, vinyl stearate, etc., 1-methylvinyl acetate, 1-ethylvinyl acetate, 1-propylvinyl acetate, 1-butylvinyl acetate, etc. and corresponding higher boiling alkanoates.

Referring to the formula hereinbefore set forth, the formula II to the right illustrates acrylates or derivatives
thereof and illustrative examples includes methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, pentyl acrylate, hexyl acrylate, octyl acrylate, capryl acrylate, lauryl acrylate, myristyl acrylate, palmityl acrylate, stearyl acrylate, etc. When R methyl, the corresponding methacrylates will comprise a component of the copolymer. Methyl methacrylate, ethyl methacrylate, propyl methacrylate, and butyl methacrylate are particularly preferred in this embodiment.

In one embodiment, the copolymer is produced by polymerization using conventional initiators of the free radical type and benzoyl peroxide, tert-butyl peroxide, di-tert-butyl peroxide, cumene peroxide, 2,2'-azobisisobutyronitrile, etc. The peroxide generally is used in a concentration of from about 0.1% to 10% and preferably 1-5% by weight of the polymeric mixture exclusive of solvent. Conveniently, a typical hydrocarbon polymerization solvent is used as, for example, benzene, toluene, xylene, heavy aromatic solvents such as xylene distillation tower bottoms (Espesol), alcohols, ketones, esters, halogenated hydrocarbons, etc. The temperature of polymerization is generally within the range of from about 250° to about 350° F. and preferably from about 275° to about 325° F. The pressure may be within the range of atmospheric to that autogenously developed when the reaction is carried out in a closed system. The time of reaction will be sufficient to accomplish the desired polymerization and may range from 1 to 12 hours or more and preferably 2 to 6 hours. However in certain cases it would be desirable to carry the reaction under pressure of an inert gas, such as nitrogen at 500 to 2000 p.s.i.g.

In one specific method of preparation of the copolymer, utilizing a rotating autoclave as the reaction zone, the autoclave is first purged with nitrogen and then charged with a solution of methyl-methacrylate in benzene, a solution of styrene in benzene, and a solution of tert-butyl peroxide in benzene. The autoclave is then closed tightly, purged with nitrogen or other inert gas, vented and again pressurized to the desired pressure, heated to the desired temperature and maintained therein for the desired time. In some cases, purging of the autoclave may be omitted and the polymerization effected in the presence of a small amount of air. Following completion of the reaction, the autoclave is allowed to cool and the products withdrawn, filtered and evaporated, preferably under vacuum, to remove solvent and to recover the copolymer. It is understood that this is a preferred method of preparing the copolymer when using the peroxide type initiator and that other suitable methods such as continuous type operation may be employed. In the continuous operation solutions containing monomers and peroxide are introduced in a reactor zone, maintained at optimum temperature. The mixture flows down and is withdrawn as a solution of the desired product.

The reactants are used in any suitable proportions. In general, the phenyl acrylate will be used in a larger mole proportion. For example, the mole ratios may comprise from 2:1 to 8:1 and preferably from 3:1 to 6:1 mole proportions of phenyl acrylate to unsaturated ester. The molecular weight of the copolymer may range from about 50 to 5000 or more and preferably from about 1000 to about 3000 and more particularly from about 1500 to about 2500.

In one embodiment, all or a major portion of the solvent is removed from the product and the copolymer is recovered as a solid material. In another embodiment, at least a substantial portion of the solvent is allowed to remain and the copolymer is recovered as a concentrated solution for use as a concentrate to be incorporated as a pour point depressant in the oil. In still another embodiment, additional solvents may be added to comprise a solution with more desirable properties for use as a pour point depressant.

As hereinbefore set forth, the copolymer is an effective pour point depressant. It is believed that styrene in admixture with the unsaturated ester forms a pour point depressant of increased solubility and of effective potency. The copolymer is incorporated in the oil in a sufficient concentration to lower the pour point of the oil to a satisfactory degree. For economical reasons, the additive is used in as low a concentration as is satisfactory for the purpose and may be within the range of from about 0.001% to about 1% but generally is within the range of from about 0.005 to about 0.1% by weight of the oil. It is understood that the pour point depressant may be used in conjunction with other, terti-butylenes peroxide incorporated in a weight percentage in 300 p.p.m. of the copolymer hydrocarbon oil and may comprise one or more of antioxidant, corrosion or rust inhibitor, viscosity, index improver, cetane improver, metal deactivator, dye, etc.

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**

This example describes the preparation of a copolymer of styrene and methylmethacrylate. The preparation was made in a 3 liter rotating autoclave. The autoclave was charged with 5 g. (0.05 mole) of methylmethacrylate in 100 g. of toluene, 26 g. (0.25 mole) of styrene in 100 g. of toluene and 1 g. (0.007 mole) of tert-butyl peroxide in 100 g. of toluene. The autoclave was purged twice with nitrogen at 70 atmospheres and then pressurized again to 70 atmospheres and heated to 284° F. and maintained at this temperature for 4 hours, after which the autoclave was allowed to cool gradually. The liquid effluent from the autoclave was filtered and evaporated under vacuum to leave 30 g. of light amber, brittle solid. The styrene to methylmethacrylate mole ratio in the copolymer is 4:4:1. The copolymer had an average molecular weight of 2200.

**EXAMPLE II**

Another copolymer is prepared in substantially the same manner as described in Example I except that benzene is used as a solvent. Specifically, the rotating autoclave is charged with 5 g. (0.05 mole) of methylmethacrylate in 100 g. of benzene, 26 g. (0.25 mole) of styrene in 100 g. of benzene and 1 g. (0.007 mole) of tert-butyl peroxide in 100 g. of benzene. The autoclave is maintained at 284° F. for 4 hours, after which the autoclave is allowed to cool and the products filtered and evaporated to remove solvent to leave the copolymer as a solid product.

**EXAMPLE III**

Another copolymer was made in substantially the same manner as described in Example I except that the mole ratio of styrene to methylmethacrylate was 3.5:1 and the autoclave was not purged with nitrogen prior to heating and reacting. It is believed that approximately 0.1 mole percent of oxygen was present in the autoclave. After cooling, filtering, evaporating to remove solvent, the copolymer was recovered as a solid product having an average molecular weight of 1500. The styrene to methylmethacrylate ratio is 3:5:1.

**EXAMPLE IV**

A copolymer is prepared in substantially the same manner as described in Example I except that the unsatu-
rated ester is vinyl acetate. The reactants are charged to the rotating autoclave in mole ratios of styrene:vynil acetate of 4:1. Following completion of the reaction and removal of the toluene solvent, the product is recovered as a solid copolymer.

**EXAMPLE V**

Another copolymer is prepared in substantially the same manner as described in Example I except that alpha-methylstyrene is used as the phenyl alkylene. The reactants are used in a mole ratio of alpha-methylstyrene:methylmethacrylate of 3:8:1. After cooling of the autoclave, filtering and vacuum distillation to remove the solvent, the copolymer is recovered as a solid product.

**EXAMPLE VI**

Another preparation was made in the same manner as described in Example I except that vacuum distillation to remove the toluene solvent is omitted and the resultant solution is utilized as a liquid concentrate for adding as a pour point depressant to a hydrocarbon oil.

**EXAMPLE VII**

The copolymer prepared as described in Example I was utilized as a pour point depressant in a commercial light cycle oil having a pour point of -2°F and a boiling range of 358–709°F. The copolymer was evaluated at three different concentrations, based on active ingredient, of 250 p.p.m. (parts per million), 100 p.p.m. and 50 p.p.m. The results of these evaluations are reported in the following table.

<table>
<thead>
<tr>
<th>Additive concentration, p.p.m.</th>
<th>Pour point, °F.</th>
<th>Pour point depression, °F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>-15</td>
<td>14</td>
</tr>
<tr>
<td>100</td>
<td>-21</td>
<td>19</td>
</tr>
<tr>
<td>50</td>
<td>-17</td>
<td>15</td>
</tr>
</tbody>
</table>

It is interesting to note that the copolymer at the intermediate concentration of 100 p.p.m. was more effective than at the higher concentration of 250 p.p.m.

**EXAMPLE VIII**

The copolymer prepared as described in Example III was evaluated as a pour point depressant in another sample of the light cycle oil described in Example VII. At a concentration of 250 p.p.m., the pour point was lowered from -2°F to -22°F. At 100 p.p.m. concentration, the pour point was lowered to -20°F. At 50 p.p.m., the concentration was lowered to -16°F.

**EXAMPLE IX**

The copolymer prepared as described in Example IV is used in a concentration of 75 p.p.m. in a commercial No. 2 fuel oil having a boiling range of 428–677°F and a pour point of 10°F. The addition of the copolymer serves to lower the pour point of the fuel oil.

**EXAMPLE X**

The flowing properties of crude oil are improved by incorporating therein 300 p.p.m. of the copolymer as described in Example I.

**EXAMPLE XI**

The pour point properties of lubricating oil are improved by incorporating therein 250–300 p.p.m. of the copolymer as described in Example IV.

1. Major amounts of an hydrocarbon oil containing hydrocarbon components which cause the oil to lose fluidity at Low temperature, said oil containing, in a pour point depressant concentration, a copolymer of styrene and methylethymacrylate in a mole ratio of styrene to methylethymacrylate of from 2:1 to 8:1, said copolymer having a molecular weight of from about 50 to about 5000.

2. The composition of claim 1 further characterized in that the mole ratio of styrene to methylethymacrylate in the copolymer is 4:1 and the copolymer has an average molecular weight of 2400.

3. The composition of claim 1 further characterized in that the mole ratio of styrene to methylethymacrylate in the copolymer is 3:5:1 and the copolymer has an average molecular weight of 1500.

4. The hydrocarbon oil of claim 1 being middle distillate within the boiling range of from about 250°F to about 750°F.

5. The hydrocarbon oil of claim 1 being lubricating oil.

6. The hydrocarbon oil of claim 1 being residual oil having an initial boiling point of at least 600°F.

7. The hydrocarbon oil of claim 1 being reduced crude oil.

8. The hydrocarbon oil of claim 1 being crude oil.

References Cited

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WARREN H. CANNON, Primary Examiner

U.S. Cl. X.R.