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MIDDLE DISTILLATE

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3 Claims

ABSTRACT OF THE DISCLOSURE

Middle distillate of improved pour point containing a pour point depressant amount of a C_{14} – C_{26} saturated carboxylic acid ester of a polyhydric alcohol having from 4 to 8 hydroxyl groups.

BACKGROUND OF THE INVENTION

Middle distillates are defined as petroleum distillates containing components boiling above the range of gasoline and having an end boiling point of not above about 750° F., and are so defined in the present specification and claims. In one embodiment the middle distillate also may include components boiling within the gasoline range and, in this embodiment, the middle distillate will boil within the range of from about 250° to about 750° F. In another embodiment the middle distillate will have an initial boiling point above gasoline and thus will boil within the range of from about 400° to about 750° F.

The middle distillate is a liquid mixture of hydrocarbons and, upon cooling, some of them crystallize to form a waxy precipitate. These crystals become active centers for further crystallization, with the result that the distillate congeals and loses its free flowing properties. The temperature at which this occurs is defined as the pour point and is of importance to petroleum refiners and users of the oil in order that the distillate may be pumped or syphoned readily for transportation or use.

Various means have been proposed heretofore to improve the pour point properties of the middle distillates. In one method this has taken the form of additional processing steps at the refinery, such as solvent extraction to remove the components believed to cause crystallization. In another method various additives have been proposed, originally based upon those which have been found effective in lubricating oils. However, it has been found that pour point depressants which are satisfactory in lubricating oils are not generally effective in middle distillates.

DESCRIPTION OF THE INVENTION

As hereinbefore set forth, the middle distillate will be within the boiling range of from about 250° to about 750° F. Illustrative middle distillates include kerosene, fuel oil, diesel oil and other middle distillates used for combustion or as cleaning oils for cleansing metallic equipment. In another embodiment the middle distillate is an electrical insulating oil which is used in transformers, circuit breakers, etc. In still another embodiment the middle distillate may comprise a conventional hydraulic oil. In still another embodiment the middle distillate may comprise an intermediate oil which is awaiting further processing as, for example, light cycle oil from catalytic cracking is being stored or transported prior to recycle to the catalytic cracking or sent to another process.

Regardless of the particular middle distillate, it is readily apparent that the distillate must be free flowing at all temperatures encountered in the transportation, storage and use thereof. The pour point properties of the

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middle distillate are improved in accordance with the present invention by incorporating a particular carboxylic acid ester of a particular polyhydric alcohol.

In one embodiment the present invention relates to a middle distillate of improved pour point containing a pour point depressant amount of a C_{14} – C_{26} saturated carboxylic acid ester of a polyhydric alcohol having from 4 to 8 hydroxyl groups.

In a specific embodiment the present invention relates to fuel oil containing sorbitan tristearate.

In another specific embodiment the present invention relates to fuel oil containing pentaerythritol monostearate.

As hereinbefore set forth, the pour point properties of the middle distillate are improved by incorporating therein a particular carboxylic acid ester of a particular polyhydric alcohol. The particular carboxylic acid used in forming the ester must be a saturated acid having from about 14 to about 26 carbon atoms. As will be illustrated in the appended examples, ester formed from unsaturated acid was found to be ineffective for the purpose. Also, the ester prepared from C_{12} fatty acid was ineffective. Saturated carboxylic acids containing 14 to 26 carbon atoms include tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, eicosanoic acid, heneicosanoic acid, docosanoic acid, tricosanoic acid, tetracosanoic acid, pentacosanoic acid and hexacosanoic acid. The acid preferably is straight chain but may contain one or two lower (1 to 4 carbon atoms) side chains. Conveniently these acids are derived from fatty acids and thus include myristic, palmytic, stearic, arachidic, behenic, lignoceric and cerotic. A number of these acids are available commercially as a mixture and, as another advantage to the present invention, the lower cost mixed acids may be used in preparing the ester for use in the present invention.

As hereinbefore set forth, the polyhydric alcohol contains from 4 to 8 hydroxyl groups. It was found that esters of glycol or glycerol were either of no activity or of very little activity in improving the pour point of the middle distillate. In contrast, esterification of pentaerythritol (containing 4 hydroxyl groups) produced very effective pour point depressants. Conveniently the polyhydric alcohols comprise carbohydrates and thus include glucose, fructose, mannose, galactose, allose, altrose, talose, gulose, idose, as well as disaccharides including sucrose, lactose, maltose, etc. In another embodiment the polyhydric alcohol is sorbitol and, in fact, a particularly preferred ester for use in the present invention is sorbitan stearate. During the esterification of sorbitol, cyclization occurs with the formation of a mixture of polyhydroxy 5 and 6-member oxygen-heterocyclic rings. Also useful as polyhydric alcohols are the dimers as, for example, dipentaerythritol, poly and preferably di-oxygen-heterocyclic ring compounds having 4 to 8 hydroxyl groups. Here again it is understood that a mixture of polyhydric alcohols may be used in the preparation of the ester.

The ester for use in the present invention may be obtained from any suitable source or prepared in any suitable manner. A number of sorbitan esters meeting the requirements of the present invention are available commercially as "Span 40" (sorbitan monopalmitate), "Span 60" (sorbitan monostearate), "Span 65" (sorbitan tristearate), "Armotan MS" (sorbitan monostearate), "Drustan 60" (sorbitan monostearate), "Drustan 65" (sorbitan tristearate), etc. When desired, the ester may be prepared by direct esterification of the alcohol with acid, by reaction with acid halides, by transesterification or in any other suitable manner. These methods are well known in the art and need not be described in detail herein. (Either the crude reaction product or selected

fraction thereof may be used, depending upon the effectiveness for the purpose.)

The ester formed in the above manner is incorporated in the middle distillate in a sufficient concentration to lower the pour point of the middle distillate to a satisfactory degree. The concentration of ester may be within the range of from about 0.001% to about 1% but generally is within the range of from about 0.01% to about 0.5% by weight of the middle distillate. When desired, the ester may be prepared as a solution in a suitable solvent which conveniently comprises hydrocarbon, including aromatics such as benzene, toluene, xylene, cumene, etc. or paraffins including decane, undecane, dodecane, tridecane, tetradecane, pentadecane, etc. but generally comprises a mixture such as high boiling naphtha, kerosene, a portion of the middle distillate, etc. It is understood that the ester may be used in conjunction with other additives normally added to middle distillates which additive will vary with the particular middle distillate and may comprise one or more of antioxidant, corrosion inhibitor, cetane improver, dye, metal deactivator, etc.

The following examples are introduced to illustrate the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

A number of esters were evaluated as pour point depressants in two different middle distillates as follows:

Middle distillate A is a commercial No. 2 fuel oil having an initial boiling point of 428° F. an end boiling point of 677° F., and a pour point of 15° F.

Middle distillate B is a light cycle oil from a commercial catalytic cracking unit. This distillate has an initial boiling point of 397° F., an end boiling point of 650° F. and a pour point of 10° F.

The pour points were determined by ASTM D97-57 method, which is a standard method for determining pour points. The results reported in the following table are the pour point depression, which is the difference between the pour point of the blank or control distillate (without additive) and the pour point of the distillate containing the additive, reported in ° F.

Unless otherwise indicated, the ester was incorporated in the middle distillate in a concentration of 1000 p.p.m. (parts per million) (0.1% by weight) of the middle distillate.

TABLE I

Test No.	Ester	Pour point depression	
		Distillate A	Distillate B
1.....	Sorbitan tristearate.....	35	40
2.....	Sorbitan monostearate.....	25	40
3.....	Pentaerythritol monostearate.....	30	30
4.....	Pentaerythritol distearate.....	30	30
5.....	Pentaerythritol tetrastearate.....	20	35

From the data in the above table it will be noted that the extent of pour point depression varied with the different middle distillates. Accordingly the particular pour point depressant will be selected with reference to the particular middle distillate in which it is to be used.

EXAMPLE II

The data reported in Example I were on the basis of 1000 p.p.m. of the pour point depressants. The sorbitan tristearate also was evaluated in lower concentrations. In a concentration of 500 p.p.m., the pour point depressions were 30 and 25 in distillates A and B respectively. At a

concentration of 250 p.p.m., the pour point depressions were 25° in both distillates. This demonstrates that the lesser amounts of ester were effective in these middle distillates.

EXAMPLE III

Sorbitan tristerate also was evaluated in a commercial diesel fuel oil having an initial boiling point of 377° F., an end boiling point of 655° F. and a pour point of 5° F. when used in a concentration of 1000 p.p.m., sorbitan tristearate served to effect a 20° F. pour point depression.

EXAMPLE IV

As hereinbefore set forth, the ester must be a saturated carboxylic acid ester. This is demonstrated in tests made with sorbitan monooleate and sorbitan trioleate. When these esters were evaluated in middle distillates A and B at a concentration of 1000 p.p.m. there was no depression of pour point in all cases except a 5° F. depression in distillate A when using the sorbitan monooleate.

EXAMPLE V

As hereinbefore set forth, the carboxylic acid used in preparing the ester must contain at least 14 carbon atoms. This is demonstrated in another series of tests in which sorbitan monolaurate was evaluated in a concentration of 1000 p.p.m. in distillates A and B. There was no depression in pour point in either of these evaluations. Thus, the ester formed from lauric acid (12 carbon atoms) was not effective in lowering the pour point of the middle distillate.

EXAMPLE VI

As hereinbefore set forth, the polyhydric alcohol used in forming the ester should contain at least 4 hydroxyl groups. This is demonstrated in another series of tests in which ethyleneglycol distearate, diethyleneglycol distearate, glyceryl monostearate and glyceryl tristearate were each evaluated in a concentration of 1000 p.p.m. in middle distillates A and B. The ethylene glycol distearate did effect a pour point depression of 5° F. in middle distillate B. Diethylene glycol distearate was of no benefit in either of the middle distillates. Glyceryl monostearate showed a 5° F. pour point depression in distillate B. No benefit in distillate A. Glyceryl tristearate showed a 5° F. pour point depression in distillate A and a 15° F. depression in distillate B. It is apparent that these esters are practically of no effect in reducing the pour point.

EXAMPLE VII

The ester of this example is a mixture of esters formed from a mixture of arachidic and behenic acids and sorbitol. The mixed esters are added in a concentration of 1000 p.p.m. to No. 2 fuel oil and serves to reduce the pour point thereof.

EXAMPLE VIII

Sorbitan myristate is incorporated in a concentration of 750 p.p.m. in commercial kerosene and serves to lower the pour point thereof sufficiently to avoid any pumping problems at temperatures normally encountered in the transportation of the kerosene.

We claim as our invention:

1. A fuel oil comprising a No. 2 fuel oil middle distillate and a C₁₄-C₂₆ saturated carboxylic acid ester of a polyhydric alcohol having from 4 to 8 hydroxyl groups, said ester in a pour point depressant concentration of from 0.01% to about 0.5% by weight.

2. A light cycle oil comprising a light cycle oil middle distillate and a C₁₄-C₂₆ saturated carboxylic acid ester of a polyhydric alcohol having from 4 to 8 hydroxyl groups, said ester in a pour point depressant concentration of from 0.01% to about 0.5% by weight.

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3. A fuel oil comprising kerosene and a C₁₄-C₂₆ saturated carboxylic acid ester of a polyhydric alcohol having from 4 to 8 hydroxyl groups said ester in a pour point depressant concentration of from 0.01% to about 0.5% by weight.

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