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[54] **MIDDLE DISTILLATE**
6 Claims, No Drawings

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ABSTRACT: Middle distillate of improved pour point containing a pour-point-depressant amount of a C_{14}—C_{20} saturated carboxylic acid ester of alpha-methylglucoside.

MIDDLE DISTILLATE

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 which 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 middle distillate are improved in accordance with the present invention by incorporating a particular carboxylic acid ester of alpha-methylglucoside.

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_{20} saturated carboxylic acid ester of alpha-methylglucoside.

In a specific embodiment the present invention relates to fuel oil containing alpha-methylglucoside palmitate.

In another specific embodiment the present invention relates to fuel oil containing alpha-methylglucoside stearate.

As hereinbefore set forth, the pour point properties of the middle distillate are improved by incorporating therein a particular carboxylic acid ester of alpha-methylglucoside. The particular carboxylic acid must be a saturated acid having from 14 to 20 carbon atoms. As will be illustrated in the appended examples, esters formed from unsaturated acids were found to be ineffective or substantially ineffective for the purpose. Also, the ester prepared from C_{12} fatty acid was ineffective. Similarly the ester formed from C_{22} fatty acid was substantially ineffective. Saturated carboxylic acids containing 14 to 20 carbon atoms include tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid and eicosanoic acid. The acid preferably is straight chain but may contain one or two lower alkyl (one to four carbon atoms) side chains. Conveniently these acids are derived from fatty acids and thus include myristic, palmytic, stearic and arachidic. 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 employed in preparing the ester for use in the present invention.

As hereinbefore set forth, the pour point depressant is the ester of alpha-methylglucoside which is also referred to a a pyranoside. particularly methyl-alpha-D-glucoside, is available commercially or may be prepared any suitable manner. It is prepared industrially by reacting glucose with methanol in the presence of a strong acid catalyst such as cation exchange resins in their hydrogen form. It also may be prepared by refluxing finely powdered glucose with methanol-HCl. Upon evaporating the methanol, the residue which contains acid catalyst and crude alpha-methylglucoside can economically be used directly for esterification to obtain desired pour point depressants. It is understood that alpha-methylglucoside may be prepared in any suitable manner or obtained from any suitable source for use in preparing the carboxylic acid ester.

While the present invention is directed primarily to the use of the ester of alpha-methylglucoside, it is understood that the corresponding ester of other glucosides may be used, with the understanding that the various additives are not necessarily equivalent. Other glucosides include ethyl glucoside, propyl glucoside, butyl glucoside, phenyl glucoside, tolyl glucoside, etc.

The ester may be prepared in any suitable manner. In a preferred method, it is prepared by esterifying alpha-methylglucoside with an acyl halide and particularly acyl chloride. The acyl chlorides include myristoyl chloride, palmitoyl chloride, stearoyl chloride and arachidoyl chloride. The concentrations of glucoside and acyl chloride to be used will depend upon whether the monoester or polyester is desired. When the monoester is desired these reactants will be reacted in equal mole proportions. When the diester is desired, 2 mole proportions of the acyl chloride will be reacted with one mole proportion of the glucoside. Similarly, when the tetraester is desired, the acyl chloride will be reacted in a ration of 4 mole proportions thereof per 1 mole proportion of the glucoside. In another method, the glucoside is esterified by reaction with the carboxylic acid and here again the concentrations of the reactants will be selected depending upon whether the mono- or polyester is desired.

The esterification may be effected in any suitable system. In one system the reactants are charged to an autoclave, which may be of the rocking type, rotating type, etc.; and then heated to the desired temperature, which may be within the range of from about 80° to about 200° C. In a preferred embodiment a solvent is used and may comprise any suitable solvent, including an aromatic hydrocarbon, such as benzene, toluene, xylene, ethylbenzene, diethylbenzene, cumene or mixtures thereof, or a paraffinic hydrocarbon including pentane, hexane, heptane, hexane, etc. or mixtures thereof. In another system, the reactants, including the solvent, preferably selected from those hereinbefore set forth, are subjected to reflux in a suitable zone equipped with heating means, stirring means and reflux condenser. The temperature of reflux will depend upon the particular solvent used and may range from about 80° to about 200° C.

As another improvement of the present invention, the reaction is effected in the presence of a tertiary amine and particularly a trialkyl amine, including trimethyl amine, triethyl amine, tripropyl amine, tributyl amine, triamyl amine, trihexyl amine, etc. The use of the amine serves the important purpose of decreasing the acidic reaction environment. Alpha-methylglucoside undergoes cleavage and degradation in a strong acidic environment and the tertiary amine serves to prevent

such decomposition of the glucoside. The tertiary amine may be used in any suitable concentration and may comprise from 0.5 to 5 and preferably from 1 to 2 mole proportions based on the mole proportion of the glucoside.

Following completion of the reaction, the products are worked up in any suitable manner. In one method, the reaction mixture is cooled, diluted with pentane, hexane or other solvent, filtered and evaporated, preferably under vacuum. When desired the dry residue may be extracted further with pentane, hexane or other suitable solvent in order to separate the desired derivative from the tetra-alkylamine hydrochloride which is formed when the acyl chloride is used as a reactant. Details of the various preparations are given in the appended examples, but it is understood that any suitable method of preparing the ester may be used in accordance with the present invention.

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 percent to about 1 percent but generally is within the range of from about 0.01 percent to about 0.5 percent 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 preferably 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 further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

The monopalmitate of alpha-methylglucoside was prepared as follows. A rocking autoclave was charged with 38.8 g. (0.2 mole) of alpha-methylglucoside, 55 g. (0.2 mole) of palmitoyl chloride, 30 g. (0.3 mole) of triethyl amine and 300 g. of toluene. The autoclave was sealed, heated to 130° C. and the reaction conducted for 6 hours. Following completion of the reaction, the autoclave was allowed to cool to room temperature, the products withdrawn and commingled with hexane. The mixture was filtered and subsequently dried under high vacuum on a steam bath to produce 53 g. of the monopalmitate as a tan solid.

EXAMPLE II

The dipalmitate of alpha-methylglucoside was prepared in substantially the same manner as described in example I except that the reactants consisted of 10 g. (0.05 mole) of alpha-methylglucoside, 27.5 g. (0.1 mole) of palmitoyl chloride in 100 cc. of toluene and 11.5 (0.11 mole) of triethyl amine in 100 cc. of toluene. The reaction was effected in the rocking autoclave for 6 hours at a temperature of about 130° C. Following completion of the reaction, the reaction mixture was filtered, rinsed with toluene and dried to recover 26 grams of the methylglucoside dipalmitate.

EXAMPLE III

In this preparation, the dipalmitate of alpha-methylglucoside was prepared by refluxing a mixture of 20 g. of alpha-methylglucoside, 55 g. of palmitoyl chloride dissolved in 100 g. of toluene, which previously had been warmed to 60° C., and 30 g. of triethyl amine. During the refluxing, an additional 100 g. of toluene was added dropwise over a 30-minute period. The refluxing was continued at 110° C. for 4 hours, after which the reaction mixture was allowed to cool to room temperature and then commingled with 400 cc. of hexane and refrigerated overnight. Next morning the material was allowed to come to room temperature and then filtered and dried to recover 37 g. of the dipalmitate of alpha-methylglucoside.

EXAMPLE IV

This example describes the preparation of the tetrapalmitate of alpha-methylglucoside. The rocking autoclave was charged with 10 g. of the methylglucoside, 55 g. of palmitoyl chloride in 100 cc. of toluene and 23 g. of triethyl amine in 100 cc. of toluene. The reaction was continued for 6 hours at 130°–135° C. Following completion of the reaction, the reaction mixture was allowed to cool and then was filtered, rinsed with hot toluene and dried under vacuum to produce 46 g. of product. The product was admixed with pentane, allowed to stand overnight and then was filtered and dried to recover 44 g. of the tetrapalmitate of alpha-methylglucoside.

EXAMPLE V

To prepare the monostearate of alpha-methylglucoside, a mixture of 8 g. of alpha-methylglucoside and 12.5 g. of stearoyl chloride was warmed and held at 135° under high vacuum until bubbling of HCl has ceased. In this preparation no solvent and no neutralizing agent-acceptor was used. The reaction was carried out in high vacuum for speedy removal of evolving HCl, in order to eliminate any harmful effect of the acid upon alpha-methylglucoside and its derivatives. There was recovered 18.3 g. of the monostearate of alpha-methylglucoside.

EXAMPLE VI

The distearate was prepared in substantially the same manner as described in example V except that 25 g. of stearoyl chloride was charged in the reactor flask. The reaction residue amounted to 30.2 g. which was recrystallized from acetone to yield 23.5 g. of the distearate of alpha-methylglucoside.

EXAMPLE VII

The distearate was also prepared by reacting a mixture of 8 g. of methylglucoside, 24.8 g. of stearoyl chloride, 10 g. of triethyl amine and 200 g. of toluene solvent. The reaction was effected in an autoclave at 130° C. for 6 hours. The reaction product was worked up in conventional manner to produce 26.4 g. of the distearate of alpha-methylglucoside.

EXAMPLE VIII

The distearate of alpha-methylglucoside also was prepared by refluxing 10 g. of alpha-methylglucoside, 28 g. of stearic acid, 10 g. of litharge (lead oxide) and 200 g. of diethylbenzene. The refluxing was continued for 6 hours at 180° C., during which time 1.35 cc. of water was formed. The reaction mixture was cooled to 75° C., 6 g. of calcium oxide was added with stirring and then the mixture was filtered and dried to produce 46 g. of product. The product was dissolved in hexane, decanted, filtered and dried to recover the distearate as a dark solid.

EXAMPLE IX

The tristearate was prepared in substantially the same manner as described in example V except that 19 g. of stearoyl chloride and 4 g. of methylglucoside were charged to the reaction flask. The residue after reaction amounted to 20.9 g., which was recrystallized from acetone to yield 17 g. of the tristearate.

EXAMPLE X

The tetrastearate was prepared in substantially the same manner as described in example IX except that the stearoyl chloride was used in a concentration of 25 g. After recrystallizing from acetone, 19 g. of the tetrastearate of alpha-methylglucoside were recovered.

EXAMPLE XI

A number of the esters prepared in the previous examples was evaluated as pour point depressants in two middle distillates as follows.

Middle distillate A is a commercial No. 2 fuel oil having an initial boiling point of 428°, an end boiling point of 677° and a pour point of 10° F.

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

The pour points were determined by ASTM D97–57 method, which is a standard method for such determinations. The results reported in the following table are on the basis of 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 degree Fahrenheit.

The ester was incorporated in the middle distillate in a concentration of 1000 p.p.m. (parts per million) (0.1 percent by weight) of the middle distillate.

TABLE I

Test No.	Ester	Pour Point Depression Distillate A	Distillate B
1	Monopalmitate of example I	45	45
2	Dipalmitate of example II	55	45
3	Tetrapalmitate of example IV	60	45
4	Distearate of example VII	30	20
5	Tetrastearate of example X	20	25

From the data in the above table, it will be noted that all of the esters were effective in depressing the pour points of the middle distillates. However, the different esters varied in effectiveness in the different middle distillates. Accordingly, the specific pour point depressant will be selected with reference to the particular middle distillate in which it is to be used.

EXAMPLE XII

The monopalmitate of example I, the dipalmitate of example II and the tetrapalmitate of example IV also were evaluated in a commercial diesel fuel oil having an initial boiling point of 377°, an end boiling point of 655° and a pour point of 5° F. When used in a concentration of 1000 p.p.m., these esters served to effect pour point depressions of 20°, 25° and 35° F. respectively. Accordingly, in this diesel fuel, the tetrapalmitate is preferred.

EXAMPLE XIII

As hereinbefore set forth, the ester must be a saturated carboxylic acid ester. This is demonstrated in tests made using the dioleate or the diricinoleate of alpha-methylglucoside in the middle distillates described in example XI and in the diesel fuel described in example XII. The dioleate and the diricinoleate were prepared in substantially the same manner as described in the previous examples. When utilized in a concentration of 1000 p.p.m., there was no depression of pour point in the evaluations using the dioleate and there was only a 5° F. depression in pour points when using the diricinoleate.

EXAMPLE XIV

As hereinbefore set forth, the carboxylic acid moiety must contain from 14 to 20 carbon atoms. In another evaluation made in substantially the same manner as described above, the dilaurate of alpha-methylglucoside did not effect any depression in the pour points of the middle distillates or diesel fuel oil. It will be noted that lauric acid contains 12 carbon atoms.

EXAMPLE XV

In a similar manner, the dibehenate of alpha-methylglucoside was evaluated. There was no improvement in pour points in the case of middle distillate B and the diesel fuel oil and only a 5° F. pour point depression in distillate A. It will be noted that behenic acid contains 22 carbon atoms and thus is outside of the range being herein claimed.

I claim as my Invention:

1. Middle distillate of improved pour point containing a pour-point-depressant concentration of a C_{14}—C_{20} saturated carboxylic acid ester of glucoside.

2. The middle distillate of claim 1 wherein said glucoside is alpha-methylglucoside.

3. The middle distillate of claim 1 wherein said concentration is from about 0.001 percent to about 1 percent by weight.

4. The middle distillate of claim 2 wherein said concentration is from about 0.01 percent to about 0.5 percent by weight.

5. The middle distillate of claim 2 wherein said ester is alpha-methylglucoside palmitate.

6. The middle distillate of claim 2 wherein said ester is alpha-methylglucoside stearate.

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