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[54] **MIDDLE DISTILLATE**

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[*] Notice: The portion of the term of this patent subsequent to Aug. 1, 1989, has been disclaimed.

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Related U.S. Application Data

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[52] **U.S. Cl.** **44/66**

[51] **Int. Cl.** **C10l 1/18**

[58] **Field of Search** ..... 44/66, 71; 252/51.5 A; 260/561 B

[56] **References Cited**

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[57] **ABSTRACT**

Middle distillate of improved pour point containing a pour point depressant concentration of the amidization reaction product of N,N-dialkylamine having 16 to 18 carbon atoms in each alkyl and hydroxy-containing carboxylic acid having 2 to 22 carbon atoms.

10 Claims, No Drawings

MIDDLE DISTILLATE

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation in part of application Ser. No. 17,860 filed Mar. 9, 1970, now U.S. Pat. No. 3,681,038.

BACKGROUND OF 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°F. 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 370°F. or 400°F. 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 temperture at which this occurs is defined as the pour point and is of importance to petroleum refiners and users of othe 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 refiners, 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°F. 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 cleaning 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 therein a particular reaction product.

Parent application Ser. No. 17,860 is directed to the use of N,N-dialkylricinole amides as pour point depressants and demonstrates the unique properties thereof to lower the pour points of middle distillates. Now it has been found that other hydroxy-containing carboxylic acids may be reacted with the N,N-dialkylamine to form a mixture of products containing a substantial amount of the amide and that these reaction products are of high effectiveness as pour point depressants.

In one embodiment the present invention relates to a middle distillate of improved pour point containing a pour point depressant concentration of the amidization reaction product of a N,N-dialkylamine having 16 to 18 carbon atoms in each alkyl and a hydroxy-containing carboxylic acid having 2 to 22 carbon atoms.

In a specific embodiment, the present invention relates to fuel oil containing the amidization reaction product of N,N-ditallowamine and hydroxybutyric acid.

Based on an extensive research study, it appears that the N,N-dialkylamine containing chiefly 16 to 18 carbon atoms in each alkyl is unique as a reactant in forming the improved reaction product with the hydroxy-containing carboxylic acid. Also, as will be demonstrated in the appended examples, the hydroxy-containing carboxylic acid offers exceptional advantages for use as a reactant in preparing the reaction product.

The reaction product will contain a substantial proportion of the amide, resulting from the reaction of the amine and acid. However, the reaction product also may contain an ester, which apparently is formed by the esterification reactions between hydroxyl group of acyl alkyls and carboxylic group of the acids. In addition, the reaction product may contain some salt and unreacted amine or acid which may result from the use of an excess of stoichiometric amounts. From a practical consideration, the pour point depressant must be marketed at a comparatively low price. Accordingly, the economics do not warrant the further time and cost necessary to insure complete reaction to the amide and/or in isolating a substantially pure amide product, especially since the amide reaction product formed under less expensive conditions is highly effective for the purpose.

As hereinbefore set forth, exceptionally good results have been obtained when using a N,N-dialkylamine having 16 to 18 carbon atoms in each alkyl as a reactant in preparing the reaction product. While the reaction product prepared from other N,N-dialkylamines do possess some pour point depressant properties, the effectiveness thereof is considerably lower than the reaction product prepared from the dialkylamine having 16 to 18 carbon atoms in each alkyl.

In a preferred embodiment, the N,N-dialkylamine for use as a reactant is N,N-ditallowamine and more particularly hydrogenated N,N-ditallowamine. The N,N-ditallowamine predominates in alkyl groups containing 16 to 18 carbon atoms, although it may contain a minor amount of alkyl groups of 14 to 20 carbon atoms per molecule. The N,N-ditallowamine and the hydrogenated ditallowamine are available commercially and advantageously are used in preparing the reactant product.

While the N,N-ditallowamine is preferred because of ready availability and comparatively low cost, it is understood that other suitable N,N-dialkylamines may be

used. In a preferred embodiment illustrative examples include N,N-dihexadecylamine, N,N-diheptadecylamine, N,N-dioctadecylamine and mixtures thereof. Conveniently the alkyl groups are derived from fatty acids as in N,N-dipalmitylamine, N,N-distearylamine and mixtures thereof, or from the corresponding unsaturated fatty acids followed by hydrogenation. It is understood that the differently substituted amines are not necessarily equivalent for use in forming the reaction product.

As hereinbefore set forth, the N,N-dialkylamine is reacted with a hydroxy-containing carboxylic acid having 2 to 22 carbon atoms. Illustrative acids include hydroxyacetic acid, hydroxypropionic acid, hydroxybutyric acid, hydroxyvaleric acid, hydroxycaproic acid, hydroxycaprylic acid, Hydroxypelargonic acid, hydroxycapric acid, hydroxylauric acid, hydroxymyristic acid, hydroxypalmitic acid, hydroxystearic acid, hydroxyarachidic acid, hydroxybehenic acid, hydroxydecylenic acid, hydroxystillingic acid, hydroxydodecylenic acid, hydroxypalmitoleic acid, hydroxyoleic acid, hydroxypetroselinic acid, hydroxyvaccenic acid, hydroxylinoleic acid, hydroxyeleostearic acid, hydroxyparinaric acid, hydroxygadoleic acid, hydroxyarachidonic acid, etc. In one embodiment, the hydroxyl group is attached to a terminal carbon atom and, in another embodiment it is attached in the chain as, for example, in ricinoleic acid, lactic acid, etc. In still another method the reaction product is prepared by the reaction of a precursor compound as, for example, a lactone as illustrated by gamma-butyrolactone, gamma-valerolactone, etc.

The reaction product is prepared in any suitable manner. The reaction is conducted under conditions to effect substantial formation of the amide and is defined herein as amidization conditions or as the amidization reaction product. This means that the hydroxyl group of the acid reacts with the hydrogen of the amine to liberate water. The temperature to be employed will depend upon the pressure and upon the solvent when employed. At ambient pressure, the temperature may range from about 175°F. to about 450°F. and correspondingly lower when effected under vacuum and thus may range from about 120°F. to about 400°F. In one method the reaction is effected by refluxing the acid and amine preferably in the presence of a solvent. When utilizing benzene solvent, the temperature may be in the range of from 170°F. to 190°F. With toluene, the temperature may be within the range of from 225°F. to 250°F. With xylene, the temperature may be in the range of from 280°F. to 310°F. With diethylbenzene, the temperature will be in the range of 350°F. to 400°F. With n-dodecane, the temperature may be within the range of from 400°F. to 450°F. These are only typical temperatures utilized at ambient pressure and will vary with the particular pressure employed and also as to whether the solvent is a mixture of isomers and/or other compounds.

Any suitable solvent is used and includes aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, diethylbenzene, cumene or mixtures thereof, paraffinic hydrocarbons such as n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, etc. or a mixture thereof, or a mixture of paraffinic and/or naphthenic hydrocarbons including some of the middle distillates such as diesel oil, No. 2 fuel oil, light cycle oil or other mixtures.

The reflux zone preferably is equipped with heating means, stirring means and reflux condenser. In another embodiment the reaction is effected in an autoclave, which is arranged to provide suitable mixing, heating and can be operated under autogenous, reduced or elevated pressure.

As hereinbefore set forth, the reaction is effected under conditions to prepare a substantial proportion of the amide product. Accordingly, the time of reaction will be determined by the amount of water collected, which then may be correlated with the amount of amide formed, allowing for ester formation resulting from the interaction of alcoholic and carboxylic moieties. The time of reaction may range from 4 to 50 hours or more. The reaction preferably is effected using equal molar proportions of acid and amine, although an excess of one or the other may be used to insure complete reaction. The reaction preferably is effected in the presence of a catalyst and conveniently comprises a resino-sulfonic acid such as "Amberlist 15". It is understood that any suitable acidic catalyst may be used. In another embodiment, particularly when the reaction is being conducted in an autoclave, a small amount of mineral acid and particularly hydrochloric acid may be used. In still another embodiment, the hydrochloride of the amine may be preformed and the acidic catalyst introduced in this manner.

Following completion of the reaction, the products are worked up in any suitable manner. In one method the reaction products are filtered to remove the catalyst. The filtering may be effected an an elevated temperature and especially when the cooled product is solid at room temperature. Following removal of the catalyst, the product may be completely evaporated to yield a solid salt but preferably is only partially dried to remove light volatile material. In many cases a solution of the product in the solvent used in the reaction medium is more convenient for use because it simplifies incorporating the product into the middle distillate.

The reaction product 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 the pour point depressant 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 the solvent previously has been removed from the reaction product or when additional solvent is desired, any suitable solvent may be employed. The solvent conveniently comprises hydrocarbons, 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 naphtha, kerosene, middle distillate, etc. It is understood that the amide 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

N,N-ditallow-ricinoleamide was prepared by refluxing 15 g. (0.05 mole) of ricinoleic acid, 25 g. (0.05

mole) of N,N-ditallowamine in the presence of 200 g. of diethylbenzene solvent and about 2 g. of "Amberlist 15" resin. The N,N-ditallowamine is hydrogenated and available commercially under the tradename of "Armeen 2HT". This amine predominates in C_{16}–C_{18} alkyl groups. The mixture was refluxed at 362°F. for about 13 hours. The water liberated in the reaction amounted to 0.9 cc. Following completion of the reaction, the effluent products were filtered and evaporated in vacuo. There were recovered 39.5 g. of product which contained 47% of N,N-ditallow-ricinoleamide.

EXAMPLE II

The reaction product of this example comprises N,N-ditallow-hydroxyacetamide and was prepared by refluxing 50 g. (0.1 mole) of "Armeen 2HT" and 8 g. (0.1 mole) of glycolic acid in 350 cc. of xylene and 2 g. of "Amberlist 15" resin. The mixture was refluxed at 284°F. for 24 hours, during which time 1.8 cc. of water was collected. The reaction product was filtered hot and then dried to produce 52 g. of product which contained 78% by weight of the amide.

EXAMPLE III

The product of this example comprises N,N-ditallow-hydroxypropionamide and was prepared in substantially the same manner as described in the previous examples. In this preparation, a mixture of 50 g. (0.1 mole) of "Armeen 2HT", 11 g. (0.1 mole) of 85% lactic acid, 205 g. of diethylbenzene and 2 g. of "Amberlist 15" resin was refluxed at 358°F. for 11 hours, during which time 6 cc. of water was collected. The product comprises 54 g. of a light tan solid.

EXAMPLE IV

A reaction product comprising N,N-ditallow-hydroxybutyramide was prepared by refluxing a mixture of 25 g. (0.05 mole) of "Armeen 2HT", 4.5 g. (0.05 mole) of gamma-butyrolactone, 2 g. of "Amberlist 15" resin and 450 cc. of diethylbenzene. The mixture was refluxed at 356°F. for 53 hours, at which time 0.9 cc. of water was collected. Following filtering and drying, 27 g. of solid product was recovered, which contained 45.6% by weight of N,N-ditallow-hydroxybutyramide.

EXAMPLE V

Additional reaction products were prepared in substantially the same manner as described in the previous examples by reacting "Armeen 2HT" separately with caprolactone and hydroxystearic acid.

EXAMPLE VI

The reaction product comprising N,N-ditallow-ricinolamide also was prepared by reacting 0.05 moles "Armeen 2HT" with 0.05 moles ricinoleic acid in toluene solvent. This reaction was effected in a 1000 cc. rocking autoclave at 392°F. for 6 hours.

EXAMPLE VII

The reaction product comprising N,N-ditallow-ricinolamide, prepared as described in Example I, was evaluated as a pour point depressant in three 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 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°F., an end boiling point of 650°F. and a pour point of 10°F.

Middle distillate C is 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.

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 °F.

The amide was incorporated in the middle distillate in a concentration of 1000 ppm (parts per million).

TABLE I

Test No.	Middle Distillate	Pour Point Depression, °F.
1	A	50
2	B	40
3	C	45

From the data in the above table, it will be seen that the ricinoleamide was very effective in depressing the pour points of all of the middle distillates. This high effectiveness in each of the three different middle distillates is unusual and demonstrates the unique effectiveness of the ricinolamide as a pour point depressant.

EXAMPLE VIII

The reaction products prepared according to Examples II, III, IV and V also were each separately evaluated in a concentration of 1000 ppm in the middle distillates described in Example VII.

The results of these evaluations are reported in the following table.

TABLE II

Test No.	Acid Moiety	Pour Point Depression, °F. Distillate A	Distillate B	Distillate C
4	Hydroxyacetic Example II	70	50	0
5	Hydroxypropionic Example III	65	45	5
6	Hydroxybutyric Example IV	70	40	30
7	Hydroxycaproic Example V	60	40	5
8	Hydroxystearic Example V	65	55	55

From the above data it will be seen that the reaction products prepared in accordance with the present invention were very effective pour point depressants in middle distillates A and B. Except as noted in the table, the reaction products were of substantially no benefit in middle distillate C. However, the amides prepared from hydroxybutyric and from hydroxystearic acid and also from ricinoleic acid (Example VII) were very effective in middle distillate C.

EXAMPLE IX

A number of corresponding amides were prepared by using the acid as reactant instead of the hydroxy acid. These amides were prepared in substantially the same

manner as described in the previous examples and also were evaluated in the same manner as described in Example VII.

The results of these evaluations are reported in the following table.

TABLE III

Test No.	Acid Moiety	Pour Point Depression, °F. Distillate A	Distillate B	Distillate C
9	Acetic Acid	0	0	0
10	Butyric Acid	0	0	0
11	Caproic Acid	0	0	0
12	Palmitic Acid	0	0	5
13	Oleic Acid	5	15	5

From the data of the above table, it will be seen that the amide prepared from these acids not containing the hydroxyl substituent were of substantially no effectiveness as pour point depressants. In contrast, as seen by the data in Example VIII, the corresponding reaction products from hydroxy acids or precursor were very effective pour point depressants.

I claim as my invention:

1. Middle distillate of improved pour point containing in combination therewith a pour point depressant concentration of the amidization reaction product of N,N-dialkylamine having 16 to 18 carbon atoms in each alkyl and hydroxy-containing carboxylic acid in which hydroxyl group is attached to the terminal carbon atom, said carboxylic acid having 2 to 22 carbon atoms.

2. The middle distillate of claim **1** in which said reaction product is prepared by reacting at a temperature of from about 175°F. to about 450°F. for a time of from about 4 to about 50 hours.

3. The middle distillate of claim **1** in which said N,N-dialkylamine is N,N-ditallowamine.

4. The middle distillate of claim **1** in which said N,N-dialkylamine is hydrogenated N,N-ditallowamine.

5. The middle distillate of claim **4** in which the reaction product comprises N,N-ditallow-hydroxyacetamide.

6. The middle distillate of claim **4** in which the reaction product comprises N,N-ditallow-hydroxypropionamide.

7. The middle distillate of claim **4** in which the reaction product comprises N,N-ditallow-hydroxybutyramide.

8. The middle distillate of claim **4** in which the reaction product comprises N,N-ditallow-hydroxycaproamide.

9. The middle distillate of claim **4** in which the reaction product comprises N,N-ditallow-hydroxystearamide.

10. The middle distillate of claim **1** in which said concentration is from about 0.001% to about 1% by weight.

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