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MIDDLE DISTILLATE

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6 Claims

ABSTRACT OF THE DISCLOSURE

Middle distillate of improved pour point containing a pour-point depressant concentration of an N,N-dialkyl-ricinoleamide in which at least one of the alkyls contains from about 12 to about 26 carbon atoms.

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 coagulates 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 transformer, 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 dis-

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tillate are improved in accordance with the present invention by incorporating a particularly substituted ricinoleamide.

In one embodiment the present invention relates to a middle distillate of improved pour point containing a pour point depressant concentration of an N,N-dialkyl-ricinoleamide in which at least one of the alkyls contains from about 12 to about 26 carbon atoms.

In a specific embodiment, the present invention relates to fuel oil containing N,N-ditallow-ricinoleamide.

The N,N-ditallow-ricinoleamide, for example, appears outstanding for use as a pour point depressant. Apparently this unique property is due to a mutually interrelated effect of the substitutions on the nitrogen atom and the hydroxy group. Regardless of the reason therefor, it has been found that the N,N-ditallow-ricinoleamide is outstanding for this use.

In a preferred embodiment the pour point depressant is an N,N-dialkyl-ricinoleamide in which both of the alkyls contain from about 12 to about 26 carbon atoms. As hereinbefore set forth a particularly preferred compound is N,N-ditallow-ricinoleamide. In another but not necessarily equivalent embodiment, the alkyl groups each contain from about 12 to about 26 carbon atoms and thus will be selected from dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl and hexacosyl. Conveniently the alkyl groups are derived from fatty acids and thus will be selected from lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric and cerotic. In still another embodiment the alkyl groups comprise mixtures as contained in various fats and oils including particularly tallow which predominates in 16-18 carbon atom molecules. Other fats and oils include palm oil, coconut oil, hydrogenated fish oil, peanut oil, lard, neat's foot oil, mutton tallow, etc. In one embodiment the fat or oil is subjected to hydrogenation in order to reduce unsaturation.

While it is preferred that the substitutions on the nitrogen atoms are saturated, it is understood that in another embodiment the unsaturated fatty acids or the fats and oils containing the unsaturated fatty acids may be used but not necessarily with equivalent results.

In another embodiment one of the alkyl groups attached to the nitrogen atom may contain less than 12 carbon atoms but the other alkyl group must contain at least 12 carbon atoms. The alkyl groups of less than 12 carbon atoms may comprise methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl and undecyl. The other alkyl group will be selected from the alkyl groups containing at least 12 carbon atoms as hereinbefore set forth. Here again, it is understood that such compounds are not necessarily equivalent to the compounds containing both alkyl groups of at least 12 carbon atoms.

The N,N-dialkyl-ricinoleamide is prepared in any suitable manner. In one method it is prepared by refluxing ricinoleic acid and the N,N-di-alkyl amine, preferably in the presence of a solvent. The reflux temperature will depend upon the particular solvent and may range from about 80° C. and preferably from about 120° C. to about 200° C. or more. For example, when using diethyl benzene as the solvent, the reflux temperature will be of the order of 180°-190° C. Any suitable solvent is used and includes aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, diethylbenzene, cumene, or mixtures thereof, or a mixture of paraffinic and naphthenic hydrocarbons, including some of middle distillates such as diesel oil, fuel oil #2, light cycle oil and 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 pro-

vided with stirring means, heating means and can be operated under elevated or reduced pressure.

Properly formulated reaction mixture, dissolved in a middle distillate oil, being used as the reaction medium, can be effected by agitating at an elevated temperature, with provision for removal of unwanted reactions products, such as water, etc., until formation of the desired product is attained. In this type of preparation there is no need to remove the solvent. The solution of N,N-dialkyl-ricinoleamide is more convenient to use for adding to oils than solvent free product, which is usually a solid matter.

In one embodiment the ricinoleic acid is a technical grade and in another embodiment it may be a lower cost crude product. In still another embodiment the charge may comprise castor oil, which contains over 85% ricinoleic acid. However, it is understood that the different grades are not necessarily equivalent but all will produce pour-point depressants.

The reaction of ricinoleic acid and the amine preferably is effected using equal molar proportions of reactants. However, when desired, an excess of the acid or the amine may be used in order 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 catalyst. The filtering may be effected at an elevated temperature and particularly when the cooled product is solid at room temperature. Following the removal of the catalyst, the crude product can be completely evaporated to yield a solid N,N-dialkyl-ricinoleamide or it can be only partially dried to remove light volatile material, leaving N,N-dialkyl-ricinoleamide dissolved in a middle distillate which is a preferred solvent. Solution of N,N-dialkyl-ricinoleamide is more convenient for use because it simplifies blending with the middle distillates, which have to be protected from freezing and loss of flow.

The amide is incorporated in the middle distillate in a sufficient concentration to lower the pour of the middle distillate to a satisfactory degree. The concentration of amide 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 amide 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 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-di-tallow amine in the presence of 200 g. of diethyl benzene solvent and about 2 g. of "Amberlist 15" resin. The N,N-ditallow amine is hydrogenated and available commercially under the tradename of "Armeen 2HT."

This amine predominates in C₁₆-C₁₈ alkyl groups. The mixture was refluxed at 183° C. 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 dried. There were recovered 39.5 g. of N,N-ditallow-ricinoleamide.

Example II

The compound of this example comprises N,N-di(C₂₀-C₂₂ alkyl)-ricinoleamide and was prepared in substantially the same manner as described in Example I. The amine used in this example is available commercially as "Kenamine S-190" and comprises a mixture in which the alkyl groups are arachidic and behenic. The reaction was effected by refluxing 30 g. (0.1 mole) of ricinoleic acid, 60.6 g. (0.1 mole) of "Kenamine S-190," 300 cc. of diethyl benzene and about 5 g. of "Amberlist 15." The mixture was refluxed at 184° C. for 10 hours. The water produced amounted to 1.7 cc. Following completion of the reaction, the reaction products were cooled to 100° C. and filtered to remove catalyst, following which the mixture was dried to produce 88.5 g. of N,N-dialkyl-ricinoleamide product as a brown solid.

Example III

N,N-ditallow-ricinoleamide is prepared by reaction of castor oil with ditallow amine in an autoclave. Unrefined castor oil 100 g. (about 0.1 mole), ditallow amine (technical grade) 150 g. (0.3 mole), "Amberlist 15" acid resin 5 g., and about 300 g. of fuel oil #2 are charged in the autoclave. The autoclave is closed and warmed to 200-230° C. and maintained for 4-6 hours, then allowed to cool and to settle. When the reaction mixture is conveniently cooled, it is decanted and filtered to yield about 50% solution of N,N-ditallow-ricinoleamide in fuel oil. The liquid product is used directly, without isolation of active ingredients.

Example IV

N,N-ditallow-ricinoleamide, 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° C., 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 p.p.m. (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

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unusual and demonstrates the unique effectiveness of the ricinoleamide as a pour point depressant.

Example V

The high effectiveness of the ricinoleamide is further demonstrated by a comparison with an amide prepared from the same amine but using palmitic acid instead of ricinoleic acid. When the N,N,ditallow-palmitylamide was evaluated in a concentration of 1000 p.p.m. each in middle distillates A, B and C, the pour point depressions were 0°, 0° and 5° F. In other words, this compound was of no benefit whatsoever in the first two middle distillates and only of very slight benefit in the third distillate.

I claim as my invention:

1. Middle distillate of improved pour point containing a pour-point depressant concentration of an N,N-dialkyl-ricinoleamide in which at least one of the alkyls contains from about 12 to about 26 carbon atoms.

2. The middle distillate of claim 1 in which both alkyls contain from about 12 to about 26 carbon atoms.

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3. The middle distillate of claim 2 in which the alkyls are derived from tallow.

4. The middle distillate of claim 3 in which the alkyls are derived from hydrogenated tallow.

5. The middle distillate of claim 1 in which the pour-point depressant is N—C₁—C₁₁-alkyl, N—C₁₂—C₂₆-ricinoleamide.

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

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