PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in and relating to Stabilized Hydrocarbon Distillates and Manufacture thereof

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised under the Laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to hydrocarbon distillates which have been stabilized against discoloration and/or sediment formation and to a novel method of achieving such stabilization.

The invention is intended to apply to hydrocarbon distillates whose boiling ranges extend at least substantially above that of gasolene, and principally includes those boiling within the range of from about 150°C. to about 400°C. These oils are marketed under various trade names such as burner oil, fuel oil, furnace oil and diesel oil, and are used principally in burner systems, diesel and combustion engines, and various other industrial and domestic equipment. Also specifically included in this classification are jet fuels and other hydrocarbon distillates containing components boiling within the range hereinbefore set forth and also containing lower boiling components. Jet fuels, for example, may have an initial boiling point as low as about 15°C. and an end boiling point within the range of from about 230°C. to about 315°C. or higher.

When in storage, most of these oils undergo deterioration of the type characterized by the formation of sediment and/or undesired discoloration. The formation of sediment is objectionable because the sediment tends to plug strainers, burner tips and injectors. Sediment contained in diesel fuel tends to form varnish and sludge in the diesel engine. Discoloration of burner oils, for example, is objectionable for various reasons, including the customer's normal preference for light colored oils.

These oils present a difficult problem because of the wide variations in stability, apparently due to the many different sources from which they are obtained. The discoloration and formation of sediment in storage varies considerably with the geographic source of the oil and with the treatment that the oil has received at the refinery. At present the oils come principally from two sources, namely non-destructive and destructive (i.e., cracking) distillation of petroleum oil. Products from the first source are called straight run distillates; and those from both non-catalytic and catalytic cracking processes are commonly referred to as cycle stocks. The latter term is used because the oil is separated from a fraction which is recycled to the cracking process for further conversion therein. Other sources of these oils may include the reaction of carbon monoxide with hydrogen in such processes as the Fischer-Tropsch Synthesis and Oxo processes. Also within the field of application of the invention are lubricating oils, transformer oils and turbine oils which undergo excessive deterioration in storage. The stability problems involved become complicated further when the oil comprises a blend of two or more different oils.

The present invention is based upon the discovery that oil deterioration of the character described can be retarded through the use of an additive which may be generally defined as a salt of a carboxylic acid and an N-alkyl alkylene polyamine, said salt containing at least 20 carbon atoms in the molecule.

The invention, accordingly, comprises hydrocarbon distillates boiling at least to a substantial extent above the gasolene boiling

[Price 3/-]

Price 4s 6d

range and having been stabilized against deterioration of the character mentioned by the addition thereto of a deterioration retardant comprising a salt of a carboxylic acid and an N-alkyl-substituted alkylene polyamine, said salt containing at least 20 carbon atoms in the molecule.

The invention also comprises a process for producing these stabilized oils, namely, a process for retarding the above mentioned deterioration of a hydrocarbon distillate boiling at least to a substantial extent above the gasoline boiling range, which comprises adding to said distillate a salt of a carboxylic acid and an N-alkyl-substituted alkylene polyamine, said salt containing at least 20 carbon atoms in the molecule.

The particular carboxylic acid and amine to be employed in preparing the additive may vary considerably depending upon the particular oil being stabilized. In general, the carboxylic acid and amine will be selected so that the salt is readily soluble in the oil in the concentrations of salt to be employed. As will be hereinafter set forth in detail, a preferred additive comprises a fatty acid salt of an N-alkyl propylene diamine, the alkyl group being derived from a fat or fatty oil.

Suitable alkylene polyamines include the N-alkyl derivatives of ethylene diamine, propylene diamine, butylene diamine, amylene diamine, hexylene diamine and homologues, as well as triamines including, for example, diethylene triamine, dipropylene triamine, dibutylene triamine and homologues, tetramines including, for example, triethylene tetramine, tripropylene tetramine, tributylene tetramine and homologues; also of other polyamines including, for example, tetraethylene pentamine and tetrabutylene pentamine. The additive should contain a sufficient number of carbon atoms for the additive to be readily soluble in the burner oil. Conveniently, a substantial portion of the carbon atoms may be included in the alkyl substituent attached to the alkylene polyamine. The preferred N-alkyl-alkylene polyamines may be illustrated by the following general formula:

$$R\text{-}NH\text{-}R'\text{-}NHR''$$

where R and R″ are selected from hydrogen and alkyl groups, at least one being an alkyl group, and where R′ is an alkylene radical. R or R″ preferably comprise an alkyl group of at least six carbon atoms and more preferably of at least 10 carbon atoms.

A particularly preferred N-alkyl alkylene polyamine comprises one in which R′ is a propylene radical, R is an alkyl group derived from tallow and R″ is hydrogen. This N-alkyl alkylene polyamine is commercially available under the registered Trade Mark "Duomeen T." Other desirable substituted propylene diamines comprise those in which R is an alkyl group derived from lauric acid, coconut oil or soya oil. The N-alkyl propylene diamines set forth above are available commercially at the present time and comprise mixed alkyl substituted propylene diamines. For example, in the case of "Duomeen T," the alkyl substituent contains from about 12 to about 20 carbon atoms per group and mostly containing 16 to 18 carbon atoms. However, when desired, the N-alkyl alkylene polyamine may be prepared to contain any number of carbon atoms desired in the R and/or R″ groups. Thus, one or both of these groups may be selected from methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, octadecyl, nonadecyl or eicosyl. It generally is preferred that one of the substituents R and R″ be hydrogen and the other an alkyl group of at least six and still more preferably of at least 10 carbon atoms. It is understood that a mixture of different amines may be employed when desired.

Any suitable carboxylic acid may be utilized in forming the additive salt and may be mono- or poly-basic. The specific carboxylic acid to be employed will be selected with regard to the particular polyamine employed, so that the resultant salt will be readily soluble in the burner oil, and thus preferably contains at least six and still more preferably at least 10 carbon atoms per molecule. The carboxylic acid may comprise formic, acetic, propionic, butyric, valeric, trimethyl acetic, oxalic, malonic, succinic, glutaric, itaconic, mesaconic, citraconic or glutaconic acid. However, it will preferably contain at least six carbon atoms, and, therefore, is advantageously selected from the following: caproic, heptylic, caprylic, adipic, pimelic, suberic, azelaic, sebacic, phthalic, capric, lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, cerotic, decylenic, dodecylenic, palmitoleic, oleic, ricinoleic, petroselinic, vaccenic, linoleic, linolenic, eleostearic, licanic, parinaric, tariric, gadoleic, arachidonic, cetoleic, erucic, selacholeic, aconitic, citric, gluconic, hemimellitic, trimellitic, trimesic, prehnitic, mellophanic, pyromellitic and mellitic acids. It is to be understood that a mixture of acids may be employed. A particularly preferred acid comprises a mixed by-product acid being marketed commercially under the trade name of "VR-1 Acid." This acid is essentially a mixture of dibasic acids and is believed to have an average of from about 35 to about 50 carbon atoms per molecule.

Another particularly preferred acid comprises tall oil acid which is a mixture of rosin acids and fatty acids and contains an average of about 16 carbon atoms per molecule.

In general, the neutral salt of the acid and amine is preferred. The neutral salt is prepared by reacting stoichiometric amounts of the acid and amine. In other words, the concentration of carboxylic acid and amine will be selected so that there will be an equivalent number of carboxylic acid groups to amino groups. Thus, the specific concentrations will depend upon whether the acid is monobasic, dibasic, tribasic or higher polybasic acid, and whether the amine is diamine, triamine or higher polyamine. In another embodiment, the salt may be a basic salt, which is prepared by utilizing a deficiency of carboxylic acid groups in relation to the amino groups, as, for example, by utilizing one equivalent of carboxylic acid per two equivalents of amine. In still another embodiment, an acid salt may be employed, which may be prepared by using an excess of acid (polybasic) with relation to the amine as, for example, two equivalents of acid per one equivalent of amine. It is to be understood that these different salts are not necessarily of equal effectiveness.

The salt may be prepared in any suitable manner and, in general, is readily prepared by admixing the acid and amine at ambient temperature, preferably with vigorous stirring. The salt is readily prepared at room temperature, although slightly elevated temperature which generally will not exceed about 93°C. may be employed when desired. Excessive temperature should not be permitted because of the formation of amides and other undesirable reaction products. Depending upon the particular amine and acid employed, it may be desirable to utilize a solvent to form a more fluid mixture of the acid and/or amine either before mixing or during the mixing thereof. In some cases it may be desirable to admix the salt with a solvent in order to form a more fluid final product. Any suitable solvent may be used and conveniently may comprise a hydrocarbon distillate.

The amount of additive to be employed will depend upon the particular salt and the oil in which it is to be used. In general, the additive will be used in a concentration of less than about 5% by weight and thus may range from about 0.0001% to about 5% by weight and still more preferably within the range of from about 0.0001% to about 1% by weight of the distillate. It is to be understood that this additive may be used along with the other additives added for specific purposes to a hydrocarbon distillate.

The following examples are introduced to illustrate further the novelty and utility of the present invention.

EXAMPLE I

The alkyl polyamine used in this example is "Duomeen T." As hereinbefore set forth "Duomeen T" is available commercially and has a theoretical molecular weight of 320 and a combining molecular weight (based on 80% active ingredient) of about 400. It is a soft paste and has a melting range of from 44°C. to 48°C. The acid used in this example is "VR-1 Acid" which, as hereinbefore set forth, is available commercially and is liquid at 25°C., has an acid number of about 150 and an iodine number of about 36. It is believed that this acid contains from about 35 to about 50 carbon atoms per molecule. As heretofore mentioned, this acid is a by-product material and, therefore, is available at relatively low cost. Because it produces a very effective additive, as will be shown in the following examples, the use of this acid is particularly attractive because of its low cost. 374 Parts by weight of "Duomeen T" are warmed moderately (at a temperature of about 52°C.) and 726 parts of "VR-1 Acid" are commingled therewith. The mixing is effected at room temperature and the mixture is vigorously stirred. A naphtha solvent having a boiling range of from about 90° to about 200°C. is added to increase fluidity.

The resultant salt is a neutral salt and was utilized for the stabilization of commercial burner oils. The burner oil samples were subjected to accelerated aging by heating at 100°C. for 20 hours, and the colors of the different samples were determined in a Lumitron, Model 402-E, spectrophotometer. Distilled water giving 100% light transmittance, is rated as 100 and a very dark oil giving substantially no light transmittance is rated as 0 in this analysis.

A commercial No. 2 (ASTM Designation D.396-48T) catalytically cracked Mid-Continent burner oil had an original color of 93.7. After accelerated aging, the color of the oil dropped to three. Salt prepared in the manner hereinbefore set forth was added to another sample of this burner oil in an amount equal to 0.005 weight per cent of the oil and, after accelerated aging, the sample had a color of 71.

It will be noted that, after the accelerated aging, the sample without additive became very dark, having a color of three, whereas the sample with additive still had a color of 71 after the accelerated aging.

EXAMPLE II

As hereinbefore set forth, one of the important objectives is that the burner oil will not clog the equipment in which it is used. This is determined in an accelerated recycle test in which a 7.57 liter sample of the oil is circulated by a gear pump at a constant rate of flow, first through a nozzle of the gun burner type having the usual screen filter and then through an edge filter having .005 cm. openings. Plugging of the filter on the nozzle is indicated by an increase in pressure on the pump discharge, while plugging of the edge filter is indicated by the development of suction on the pump intake side. The suction on the pump intake continues at nil for an interval and then shows a rapid increase, thereby simulating an induction period. The time necessary for this increase is designated as "inflection point." This test is fairly reproducible, and indicates the plugging characteristics of the oil.

The oil used in this example was a commercial West Texas No. 2 fuel oil. This oil had an original inflection point of 33 hours. Upon the addition of 0.005% by weight (based upon the oil) of the additive described in Example I, the inflection point was increased to 61. Upon the addition of 0.01% by weight of this additive to another sample of the oil, the inflection point was increased to 84 hours.

From the above data it is apparent that the additive of the present invention served to considerably prolong the inflection point of the oil and thereby to retard its plugging characteristics.

EXAMPLE III

The oil used in this example was a West Texas thermal cracked No. 2 burner oil which had an original inflection point of seven hours. Upon the addition of 0.005% by weight (based upon the oil) of the additive described in Example I, the inflection point of the oil was increased to 14 hours, thus doubling the time before plugging occurred.

EXAMPLE IV

The additive used in this example was a basic salt of "Duomeen T" and "VR-1 Acid" and was prepared by admixing two equivalents of amine per one equivalent of acid. 0.01% by weight (based upon the oil) of the additive increased the inflection point of another sample of the No. 2 burner oil described in Example II from 33 hours to 84 hours.

EXAMPLE V

The additive used in this example is "Duomeen T" dioleate prepared from "Duomeen T" and oleic acid.

0.005% by weight (based upon the oil) of this additive increased the inflection point of another sample of the No. 2 burner oil described in Example II from 33 hours to 76 hours.

EXAMPLE VI

In order to confirm the results obtained in the recycle test described in Example II, samples of the oil described in Example II were analysed according to the oil circulation method described by Rescorla, Cromwell and Milsom in "Analytical Chemistry," Vol. 24, pages 1959-1964 (December 1952). The original oil had an inflection point of 40 hours. The addition of 0.01% by weight (based upon the oil) of the additive described in Example II increased the inflection point of the oil to 72 hours.

EXAMPLE VII

An additive is prepared by commingling 186 parts by weight of "Duomeen T" and 292 parts by weight of tall oil acid.

The additive prepared in the above manner may be incorporated in a concentration of 0.02% by weight (based upon the oil) in a blended burner oil comprising a mixture of 30 volume per cent straight run distillate (Gulf Coast; boiling range 350° to 550°F.) and 70 volume per cent catalytic cycle stock (Mid-Continent; boiling range 420° to 750°F.). This will serve to retard discoloration of the oil and to reduce sediment formation therein.

EXAMPLE VIII

The polyamine used in this example is N-lauryl-1, 4-butylene diamine. The lauryl butylene diamine is admixed with stearic acid to form the corresponding salt.

The additive as prepared in the above manner is added to a commercial light catalytic cycle stock (Mid-Continent; boiling range 420° to 650°F.) in a concentration of 0.008% (based upon the cycle stock) and will serve to retard discoloration and sediment formation thereof.

EXAMPLE IX

A jet fuel comprising a mixture of equal volumes of cracked cycle stock (East Texas; boiling range 310° to 653°F.) and straight run distillate (Mid-Continent; boiling range 152° to 313°F.) may be stabilized against the above mentioned deterioration by the addition thereto of 0.01% by weight (based upon the mixture) of the lauryl butylene diamine stearate described in Example VIII.

EXAMPLE X

A Mid-Continent solvent extracted neutral lubricating oil (viscosity 180 Saybolt Universal Seconds at 130°F.) may be stabilized against the above mentioned deterioration by incorporating therein 0.5% by weight (based upon the oil) of the additive prepared in the manner described in Example I.

What we claim is:—

1. A hydrocarbon distillate boiling at least to a substantial extent above the gasoline boiling range and containing a deterioration retardant comprising a salt of a carboxylic acid and an N-alkyl-substituted alkylene polyamine, said salt containing at least 20 carbon atoms per molecule.

2. A distillate as claimed in Claim 1, characterized in that the retardant comprises a salt of a carboxylic acid and an N-alkyl-substituted propylene diamine in which the alkyl substituent contains at least 6 carbon atoms.

3. A distillate as claimed in Claim 2, further characterized in that the alkyl substituent of the propylene diamine contains from

about 12 to about 20 carbon atoms.

4. A distillate as claimed in any of the Claims 1 to 3, characterized in that the salt is a salt of a polybasic carboxylic acid.

5. A distillate as claimed in Claim 4, further characterized in that the sallt is a salt of a dibasic carboxylic acid containing from about 35 to 50 carbon atoms per molecule.

6. A distillate as claimed in Claims 4 or 5, further characterized in that the distillate contains a neutral salt of the acid and amine.

7. A distillate as claimed in Claim 4 or 5, further characterized in that the distillate contains an acid salt of the acid and amine.

8. A distillate as claimed in Claim 4 or 5, further characterized in that the distillate contains a basic salt of the acid and amine.

9. A distillate as claimed in any of the Claims 1 to 8, characterized in that the distillate contains an amount of the salt within the range of from about 0.0001% to about 5% by weight of the distillate.

10. A process for retarding the hereinbefore described deterioration of a hydrocarbon distillate boiling at least to a substantial extent above the gasoline boiling range which comprises adding to said distillate a salt of a carboxylic acid and an N-alkyl-substituted alkylene polyamine, said salt containing at least 20 carbon atoms per molecule.

11. Process as claimed in Claim 10, characterized by adding to the distillate a salt of a carboxylic acid and an N-alkyl-substituted propylene diamine in which the alkyl substituent contains at least 6 carbon atoms.

12. Process as claimed in Claim 11, further characterized in that the alkyl substituent of the propylene diamine contains from about 12 to about 20 carbon atoms.

13. Process as claimed in any of the Claims 10 to 12, characterized in that the salt is a salt of a polybasic carboxylic acid.

14. Process as claimed in Claim 13, further characterized in that the salt is a salt of a dibasic carboxylic acid containing from about 35 to about 50 carbon atoms per molecule.

15. Process as claimed in Claim 13 or 14, further characterized by adding to the distillate a neutral salt of the acid and amine.

16. Process as claimed in Claim 13 or14, further characterized by adding to the distillate an acid salt of the acid and amine.

17. Process as claimed in Claim 13 or 14, further characterized by adding to the distillate a basic salt of the acid and amine.

18. Process as claimed in any of the Claims 10 to 17, further characterized by adding to the distillate an amount of the salt within the range of from about 0.0001% to about 5% by weight of the distillate.

19. A process for retarding deterioration of a hydrocarbon distillate substantially as herein described.

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