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COLOR STABLE HEATER OILS

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6 Claims. (Cl. 44—72)

The present invention relates to improvements in heating oils derived from petroleum. More particularly, it is concerned with improved color stabilization of such oils. Still more particularly, this invention is concerned with the use of a combination of additives effective generally for stabilization against oxidative deterioration resulting in color and other undesirable effects such as gum and sediment.

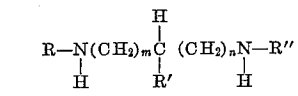
One of the most troublesome and most readily observed effects of the deterioration of petroleum heating oils is darkening of the oils, i.e., petroleum distillates boiling chiefly from about 300° F. to about 750° F., which is usually a direct result of oxidation of the oil and it has been common practice in the art to add various types of inhibitors to the oils for the purpose of inhibiting the deterioration caused by such oxidation. Among the very best inhibitors are the N-alkyl alkylene polyamines such as N-octadecyl propylene diamine and the like which are described and claimed in co-pending application for Letters Patent Serial No. 395,272 of Richards et al., filed November 30, 1953. Such N-alkyl alkylene polyamines have been found to be exceptional in their ability to inhibit sediment formation in most, if not all, petroleum heating oils. And, although for the most part, their ability to inhibit color degradation is also good, it has been found that certain oils, particularly virgin heater oil fractions and blends of virgin heater oil fractions from different crude sources at times are not adequately stabilized by such amines alone.

It has been found that virgin heater oils and other virgin distillate fuels boiling chiefly in the range of from about 375° F. to 750° F. and particularly those boiling in the range of from about 330 to 580° F. may be stabilized against color degradation caused by oxidative deterioration by the combined used of an N-alkyl alkylene polyamine of the type hereinafter described in detail and certain class of metal deactivators of the type prepared by reacting aromatic orthohydroxy aldehydes with alkyl amines. A metal deactivator of this general type is N,N'-disalicylidine-1,2-diaminopropane. Such compounds are the reaction products of an alkyl amine and an aromatic orthohydroxy aldehyde such as 2-hydroxy-benzaldehyde, 2,4-dihydroxybenzaldehyde, 2-hydroxy-3-methoxybenzaldehyde, etc. It is ,of course, very old in the art to employ metal deactivators of this type in petroleum oils generally, for the purpose of suppressing the catalytic activity of copper present in the oil. Such copper is often present as a result of a prior sweetening step employing $CuCl_2$ or the like. It has been found in accordance with the present invention, however, that oils which have not been treated with copper compounds and do not to any measurable extent contain copper in any form and which do not respond properly to the use of an N-alkyl alkylene polyamine or its carboxylic acid salt may be synergistically improved in respect to color stability by the use of a metal deactivator of the hydroxyaldehyde-amine reaction product type along with such N-alkyl

alkylene polyamine. Oils which do not respond with a reduced tendency toward color formation by either the polyamine alone or the metal deactivator alone show outstanding color stability when the two are employed together. Oils which have been copper chloride treated, of course, may also be stabilized to a high degree by the use of the combined additives.

Thus, in accordance herewith, virgin heater oils of the above-indicated boiling range which may be derived from one crude source or be blends of virgin heater oils from different crudes may be stabilized to a high degree against color degradation by the addition thereto of from about 0.00001 to about 0.01% by weight and preferably from about 0.0003 to about 0.001% of a metal deactivator of the type obtained by reacting an alkyl polyamine and an aromatic orthohydroxyaldehyde (which metal deactivators will be more fully defined hereinafter) and from about 0.0005 to about 0.1% by weight and preferably from about 0.001 to about 0.005% by weight of the oil of an N-alkyl alkylene polyamine of the type hereinafter described in detail. A typical heating oil composition of the present invention comprises a petroleum distillate heater oil fraction boiling from about 330° F. to about 580° F., which contains 0.0025% of "Duomeen T" (an N-alkyl alkylene polyamine wherein the N-alkyl group contains 18 carbon atoms and is derived from tallow fatty acid; Duomeen T is a product of Armour Chemical Division of Armour and Co.) and 0.0007% of N,N'-disalicylidine-1,2-diaminopropane.

Amines suitable for use in accordance herewith are those N-alkyl alkylene polyamines containing at least one primary amino nitrogen atom. Such amines, in general, may be represented by the structural formula:



wherein R represents an alkyl or substituted alkyl (i.e. by hydroxy, carboxy, nitro, halo-, etc. groups) hydrocarbon radical containing from about 16 to about 20 and preferably about 18 carbon atoms; R' may be hydrogen or an aliphatic hydrocarbon radical, i.e. alkyl or cycloalkyl radicals and it is preferably hydrogen; R'' may be hydrogen, an alkylene primary amino radical (i.e.—$(CH_2)_xNH_2$, wherein x is a positive integer from 1 to about 10) or a polyalkylene polyamino radical containing a primary amino nitrogen atom; m is a positive integer from 1 to about 10 and preferably 1 or 2; and n may be either 0 or a positive integer from 1 to about 10. Typical examples of such compounds are the higher alkyl derivatives of ethylene diamine, of propylene diamines (1,3-diamines (1,3-diaminopropane; 1,2-diaminopropane), of diethylene triamine, of triethylenetetramine, etc.

More specifically, there may be employed such amines as N-octadecyl-ethylene diamine, N-n-octadecyl diethylene triamine, N-n-cetyl-propylene diamine, N-octadecyl triethylene tetramine, N-hydroxy octadecyl-diethylene triamine, N-chloro-cetylethylenediamine, N-bromo octadecyl ethylene diamine, Duomeen T and Duomeen S (products of Armour Chemical Division) which have the general formula $RNHCH_2CH_2CH_2NH_2$ wherein R is derived from tallow fatty acid ("Duomeen T") and from soya fatty acid ("Duomeen S") respectively, etc. The "Duomeens" are industrial or technical grade chemicals with an amine content of approximately 80% calculated as di-amine. The approximate melting ranges for each of the aforementioned "Duomeens" are: "Duomeen S"—38° to 42° C., and "Duomeen T"—44° to 48° C. It should be understood that the enumeration of the fore-

going specific amino-compounds is by way of illustration and not of limitation and that any polyamine falling within the broad definition above recited may be employed in accordance herewith.

The salts of the polyamines which may also be employed in accordance herewith may be prepared by reacting, under carefully controlled, nondehydrating conditions, i.e., below about 200° F. and preferably below about 195° F., an aliphatic carboxylic acid containing from about 6 to about 20 carbon atoms, e.g., hexanoic, nonanoic, lauric, stearic, oleic, linolenic, palmitic, etc., with any of the hereinabove described amines to obtain either the mono- or di- substituted acid salts of the amines. Care must be taken in the preparation of such salts inasmuch as prolonged exposure to temperatures higher than about 200° F. results in the formation of amides or even glyoxalidines (if 1,2-substituted polyamines are employed) upon splitting out water. Among the very economical, commercially available salts of this type are the oleic acid mono- and/or di-salts of the Duomeens (above described), particularly of Duomeen T.

The metal deactivators which may be employed in accordance with the present invention are, as indicated above, the so-called arylidene amines or Schiff's bases obtained by condensing one mol of a polyamine containing at least two primary amino groups capable of reacting with aromatic aldehydes to form arylidene amines with at least two mols of an orthohydroxy substituted aldehyde which is aromatic in nature, so that not more than one mole of aldehyde reacts for each mol of primary amino group of the amine.

Such arylidene amines are described in detail in U.S. 2,181,121. In addition, this type of metal deactivator is further discussed in a paper by Watson et al., in Industrial and Engineering Chemistry, volume 41 (May 1949), page 918. Further description of the metal deactivators suitable in accordance herewith is not believed necessary inasmuch as it is intended that the aforementioned references be incorporated by reference to the extent necessary for a complete and detailed explanation of these compounds. However, it is believed desirable for purposes of clarity and understanding, to indicate that the metal deactivators suitable in accordance herewith may be represented by the formula

HO—A—CHN—R—NCH—A—OH

wherein A represents an aromatic ring, the OH radical is attached directly to a ring carbon atom with ortho-position with respect to the —CHN— group, and R represents an aliphatic hydrocarbon radical having the two N atoms attached directly to different carbon atoms of the same open chain of R.

For purposes of illustrating the present invention but without the intention for unduly limiting the same, the data in Table 1 are set forth to demonstrate the outstanding results obtainable in accordance herewith. The data in Table 1 refer to tests with an acid treated virgin heater oil derived from a West Texas crude. Such oil had an initial boiling point of 334°, an end point of 563° and an overall inspection as follows:

API gravity		41.8
Flash (Tcc), ° F		120
Pour, ° F		—30
ASTM distillation:		
Initial, ° F	degrees	334
10%	do	364
50%	do	428
90%	do	515
End point	do	563

Table 1

	Color (Saybolt)				
	Initial	Aged [1]			
		Control	MD [2] added	Duomeen T [3] added	MD [2] and Duomeen T [3] added
Sample 1	18	0	2	7	13
Sample 2	17	−2	−1	8	15
Sample 3	18	−4	−2	−2	13

[1] Heated for one hour at 290° F.
[2] Metal deactivator-N,N'-disalicylidene-1,2-diamino propane added to oil in amount of 2 pounds of M.D. per 1000 barrels of oil.
[3] Duomeen T is a product of Armour Chemical Division of Armour & Company; it has the formula $RNHCH_2CH_2CH_2NH_2$ where R is derived from tallow fatty acid. Duomeen T was added to the oil in an amount of 0.005% by weight.

From the above table, it is apparent that, while slight, the metal deactivator has some beneficial effect upon color stability. And the stabilizing effect of the polyamine is much greater. The joint use of the two additions results, however, in an oil substantially as stable after aging as before.

Table 2 sets forth data demonstrating the high degree of stability imparted to a heater oil comprising a blend of an acid treated West Texas virgin heater oil distillate and a copper chloride sweetened Mid-Continent virgin heater oil distillate by the use of the combination of additives of the present invention. Also demonstrated is the substantial interchangeability of the N-alkyl alkylene polyamine and its salt for the purposes thereof.

Table 2

Sample [4]:	Aged color [2]
(1) Heater oil [1] without additives	1–1½ NPA
(2) Heater oil [1] containing Duomeen T	−9
(3) Heater oil [1] containing Duomeen T monooleate	−11
(4) Heater oil [1] containing metal deactivator [3]	+6
(5) Heater oil [1] containing Duomeen T plus metal deactivator [3]	+12
(6) Heater oil [1] containing Duomeen T monooleate plus metal deactivator [3]	+11

[1] A 1:1 blend of acid treated West Texas virgin heater oil distillate and copper chloride sweetened Mid-Continent virgin heater oil distillate.
[2] All color readings in Saybolt after 1 hour's heating at 290° F. except as otherwise noted. 1–1½ NPA indicates poorer color than lowest reading on Saybolt scale.
[3] N,N', disalicylidine-1,2-diamino propane employed in amount of 2 lbs./1000 barrels (0.0007% by weight).
[4] Duomeen T and Duomeen T monooleate employed in amount of 0.005% by weight.

Heater oils sweetened by the process, e.g., the doctor process, are also stabilized with respect to color by the combination of additives of the present invention. Thus, set forth in Table 3 are long-term storage data obtained on refinery samples of doctor sweetened heater oil having the following inspection:

Gravity, ° API		42.4
Initial B.P	degrees	358
10%	do	378
50%	do	432
90%	do	515
Max	do	568
Percent recovered		98.5
Percent residue in still		1.5
Initial color		12

In the long term storage tests reflected by the data in Table 3, the samples were placed in the dark in open bottles and in contact with pieces of iron to simulate the tank walls. At monthly intervals, Saybolt color determinations were obtained.

Table 3

	Color [1] (Saybolt)			
	Months of storage			
	1	2	3	4
Control (undoped oil)	12	0	−4	−8
0.0025% Duomeen T (I)	11	7	9	5
0.0007% N,N' disalicyclidine-2,2-diaminopropane (II)	11	6	−2	−4
0.001% I plus 0.0007% II	10	10	11	
0.0025% I plus 0.0007% II	13	10	10	8
0.005% I plus 0.0007% II	8	7	10	10

[1] Initial color of heater oil was 12.

Because of the known ability of N-alkyl alkylene polyamine carboxylic acid salts to inhibit corrosion of metals in contact with oils containing the same, coupled with somewhat greater effectiveness of the amines as color degradation inhibitors as compared to the salts, it may often be desirable to employ both amine and carboxylic acid salt along with a metal deactivator of the type herein described in a heater oil. Such should be understood to fall within the scope of the present invention.

Percentages given herein and in the appended claims are by weight unless otherwise specified.

Having thus described our invention, what we claim as novel and desire to protect by Letters Patent is as follows:

1. A color stable heating oil consisting essentially of a normally color unstable blend of at least two virgin distillate fractions derived from distinct crude sources, said blend boiling in the range 300° to 750° F., and chiefly above about 375° F., from about 0.0005% to about 0.1% of an N-alkyl alkylene compound having the general formula $RNHCH_2CH_2CH_2NH_2$, wherein R is an alkyl radical containing from about 16 to about 20 carbon atoms and from about 0.00001% to about 0.01% of an oil soluble hydroxy benzaldehyde diimine having the general formula

$$HO—A—CH=N—R^1—N=CH—A—OH$$

wherein A represents an aromatic ring, the OH radical is attached directly to a ring carbon atom in the ortho-position with respect to the —C=N— group, and R^1 represents an aliphatic hydrocarbon radical having the two N atoms attached directly to different carbon atoms of the same open chain of R^1, wherein neither said N-alkyl alkylene compound nor said diimine is effective alone to produce said color stable oil.

2. The color stable petroleum heating oil of claim 1 wherein the blend comprises a distillate fraction derived from a sour West Texas crude and a distillate fraction derived from a Mid-Continent crude.

3. The color stable petroleum heating oil of claim 2 wherein the distillate fractions are blended in a ratio of 1:1.

4. A color stable heating oil consisting essentially of a normally color unstable virgin petroleum distillate oil boiling in the range 300° to 750° F. and chiefly above about 375° F., from about 0.0005% to about 0.1% of an N-alkyl alkylene compound having the general formula $RNHCH_2CH_2CH_2NH_2$ wherein R is an alkyl radical containing from about 16 to about 20 carbon atoms and from about 0.00001% to about 0.01% of an oil soluble hydroxy benzaldehyde diimine having the general formula

$$HO—A—CH=N—R^1—N=CH—A—OH$$

wherein A represents an aromatic ring, the OH radical is attached directly to a ring carbon atom in the ortho-position with respect to the —C=N— group, and R^1 wherein neither said N-alkyl alkylene compound nor said diimine is effective alone to produce said color stable oil represents an aliphatic hydrocarbon radical having the two N atoms attached directly to different carbon atoms of the same open chain of R^1.

5. The color stable heating oil of claim 4 wherein R is derived from the alkyl radical of tallow fatty acids and contains 18 carbon atoms.

6. The color stable heating oil of claim 4 wherein R is derived from the alkyl radical of tallow fatty acids and contains 18 carbon atoms and the hydroxy benzaldehyde diamine is N,N'disalicyclidine-1,2-diaminopropane.

References Cited in the file of this patent

UNITED STATES PATENTS

2,181,121	Downing et al.	Nov. 28, 1939
2,333,294	Chenicek	Nov. 2, 1943
2,364,502	Zimmer et al.	Dec. 5, 1944
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2,641,539	Thompson et al.	June 9, 1953
2,681,935	Thompson	June 22, 1954

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,906,611 September 29, 1959

Robert F. Schnaith et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 48, the formula should appear as shown below instead of as in the patent:

$$-- HO-A-CH=N-R-N=CH-A-OH --;$$

line 52, for "—CHN—" read -- —CH=N— --; line 57, for "intention for" read -- intention of --; column 4, line 66, for "Max" read -- Max. --; column 6, lines 26 and 27, strike out "wherein neither said N-alkyl alkylene compound nor said diimine is effective alone to produce said color stable oil" and insert the same after "R^1" and before the period in line 30, same column.

Signed and sealed this 26th day of April 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents