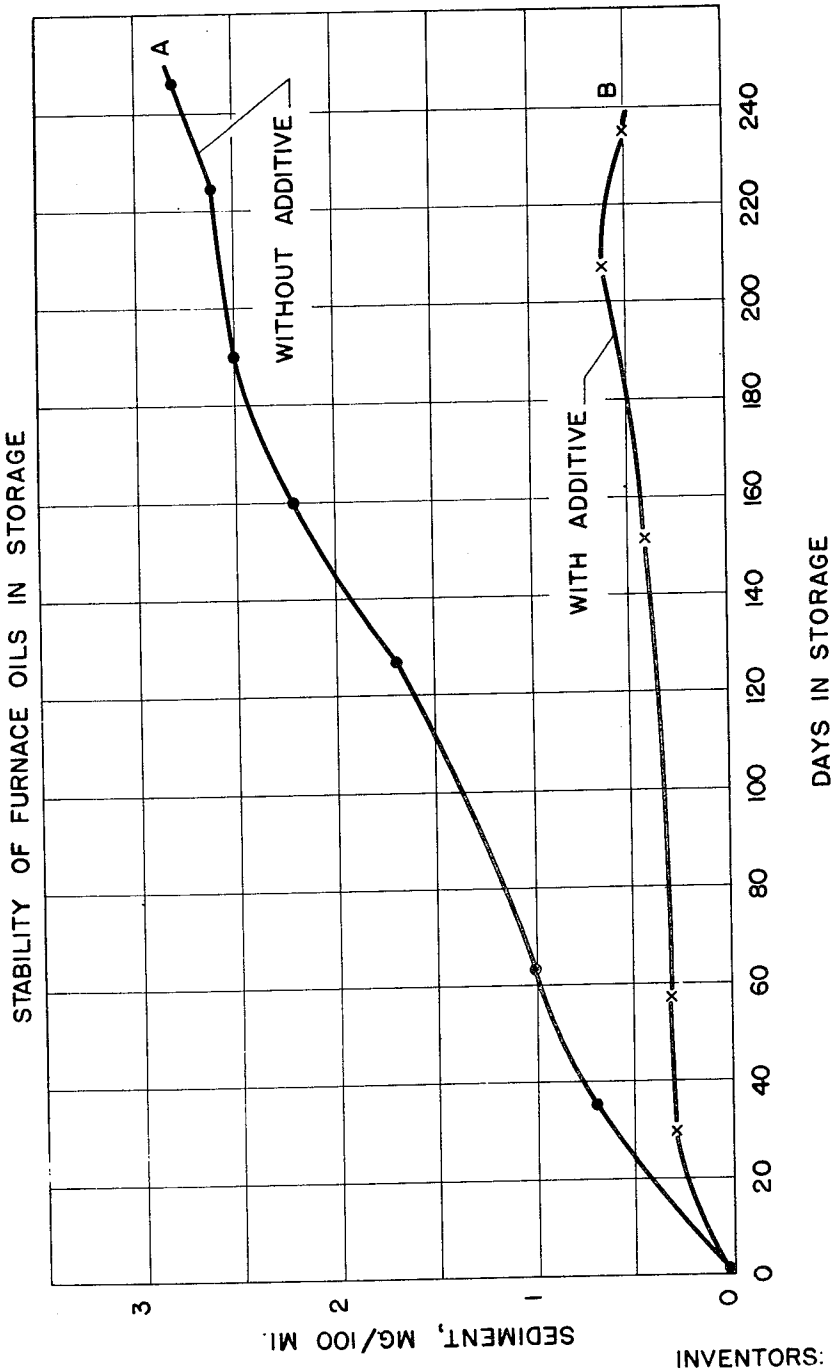
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STABILIZATION OF BLENDED BURNER OILS

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FIG. 1



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STABILIZATION OF BLENDED BURNER OILS

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17 Claims. (Cl. 44—72)

This application is a continuation-in-part of our copending application Serial No. 56,232, filed October 23, 1948, now abandoned, and relates to the stabilization of blended burner oils and more particularly to a process for retarding sediment formation and discoloration of burner oils in storage.

The term "burner oil" is used in the present application in a generic sense to include hydrocarbon distillates heavier than gasoline. In general, these hydrocarbon distillates will have initial boiling points ranging as low as 300° F. and end boiling points which may range up to about 750° F. The blended burner oil of the present invention comprises a mixture of one or more virgin or straight run petroleum distillates, one or more cracked, preferably catalytically cracked, hydrocarbon oils, and/or one or more burner oils produced from other sources.

At the present time burner oils come primarily from non-destructive distillation of petroleum oil, commonly referred to in the art as straight run distillates, and from catalytic and non-catalytic cracking processes, commonly referred to in the art as cycle stocks. The term cycle stock is used because the burner oil is separated from a fraction which is recycled to the cracking process for further conversion therein. Other sources of burner oil may include those produced by the reaction of carbon monoxide with hydrogen in the process known as the Fischer-Tropsch process. Regardless of the source, the blended burner oils tend to undergo discoloration and form sediment in storage, and the present invention is directed to a method of retarding this deterioration.

The formation of sediment in burner oil is objectionable because the sediment tends to plug strainers, burner tips, injectors, etc. and, when used as diesel fuel, tends to form varnish and sludge in the cylinders of the diesel engine. The sediment referred to herein is different from the solid material originally contained in burner oils and referred to in the art as B. S. & W. The sediment with which the present invention is concerned is not contained as such in the burner oil as produced but forms during storage.

Burner oils are marketed under various trade names such as fuel oil, furnace oil, burner oil, diesel fuels, jet fuels, etc. and are selected to meet commercial specifications. In the past, burner oils have come mostly from straight run distillates but, with the increasing amount of catalytic cracking processes being installed, a considerable quantity of catalytic cycle stock is available and is being used for burner oil. However, catalytic cycle stock generally is not of satisfactory burning qualities and cannot be used alone. Refiners have therefore adopted the practice of blending catalytic cycle stock with straight run distillate to produce a saleable burner oil. However, it has been found that blended burner oils undergo discoloration and sediment formation to an undesirable extent, and the present invention is directed to a method of retarding this deterioration.

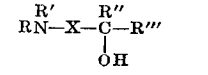
While, as hereinbefore set forth, the present invention is specifically applicable to the treatment of blends of catalytic cycle stock and straight run distillate, it is understood that the present invention may have application to the treatment of blended oils for use as lubricating oil, transformer oils, turbine oils, etc. which undergo excessive deterioration in storage.

In one embodiment the present invention relates to a process for retarding sediment formation and discoloration of a blended burner oil in storage, which comprises adding thereto a minor amount of an alkanol amine containing an alkyl group having at least 6 carbon atoms.

In another embodiment the present invention relates to a blend of straight run petroleum distillate and cracked hydrocarbon oil, both heavier than gasoline, containing, as a retardant of sediment formation and discoloration in storage, a minor amount of a primary alkanol amine of not more than 20 carbon atoms per molecule and containing an alkyl group having at least 6 carbon atoms.

In still another embodiment the present invention relates to a blend of straight run petroleum distillate and catalytically cracked hydrocarbon oil, both heavier than gasoline, containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 0.1% by weight of a primary alkanol amine of not more than about 20 carbon atoms per molecule and in which the amino group and the hydroxyl group are attached to adjacent carbon atoms of an alkyl group containing at least 6 carbon atoms in straight chain arrangement.

The alkanol amine for use in the present invention will have the following general structure:



where X is an aliphatic group containing at least 1 carbon atom and where R, R', R'', and R''', are selected from the group consisting of hydrogen and alkyl groups. In its preferred embodiment it is an essential limitation that the alkanol amine contains at least 6 carbon atoms. Preferably the alkanol amine will not contain more than about 20 carbon atoms per molecule. It has been found that the alkanol amines containing less than 6 carbon atoms per molecule are not sufficiently soluble in burner oils to be satisfactory for use. On the other hand, alkanol amines containing more than about 20 carbon atoms per molecule will be too heavy for satisfactory use.

In another preferred embodiment, it is essential that the amino group and the hydroxyl group are attached to adjacent carbon atoms. It has been found that in general, alkanol amines containing this configuration are outstanding in their potency to retard sediment formation and discoloration of burner oils in storage.

In another preferred embodiment, the alkanol amine is preferably a primary alkanol amine and this is defined as an alkanol amine in which the amine group is a primary amine; that is, two hydrogen atoms are attached to the nitrogen atom.

A particularly preferred primary alkanol amine for use in the present invention comprises 5-amino-4-octanol. Other preferred alkanol amines include 1-amino-2-hexanol, 2-amino-3-hexanol, 2-amino-2-methyl-3-hexanol, 3-amino-4-hexanol, 2-amino-1-hexanol, 3-amino-2-hexanol, 1-amino-2-heptanol, 2-amino-3-heptanol, 3-amino-4-heptanol, 2-amino-1-heptanol, 3-amino-2-heptanol, 4-amino-3-heptanol, 1-amino-2-octanol, 2-amino-3-octanol, 2-amino-2-methyl-3-octanol, 3-amino-4-octanol, 2-amino-1-octanol, 3-amino-2-octanol, 4-amino-3-octanol, etc. It will be noted that the alkanol amines herein set forth are compounds in which the amino group and the hydroxyl group are attached to adjacent carbon atoms. As hereinbefore set forth, alkanol amines containing this structure are particularly preferred for use in the present invention.

Included within the broad scope of the present invention but not necessarily with equivalent results are alkanol amines containing, in addition to the amine and hydroxyl groups, substituents such as sulfur, nitrogen or oxygen atoms or groupings, such as amino, nitro, nitroso, alkylaminoalkyl, dialkylaminoalkyl, hydroxyl, hydroxyalkyl, ether groups, etc. It is understood that the total number of carbon atoms in the molecule shall not exceed about 20 as hereinbefore set forth. Similarly salts of these alkanol amines with carboxylic acids may be employed within the broad scope of the present invention. In these cases however the number of carbon atoms should be at least 12 in order that the salt will be sufficiently soluble in the burner oil for satisfactory use. Another modification for use in accordance with the present invention

comprises saturated ring compounds containing both an amino group and a hydroxyl group attached thereto.

The preferred primary alkanol amines for use in the present invention may be prepared in any suitable manner. One satisfactory method for the preparation of 5-amino-4-octanol is to react nitrobutane with butyraldehyde in the presence of a base, such as sodium hydroxide, sodium methylate, trimethylbenzyl ammonium hydroxide, etc., and to reduce the product, preferably catalytically, to form the desired 5-amino-4-octanol.

The alkanol amines are added to burner oils in amounts up to about 1% by weight and preferably in an amount of from about 0.0005% to about 0.1% and more particularly from about 0.005% to about 0.05% by weight. It is understood that these alkanol amines may be used in conjunction with other additives, such as metal deactivators, antioxidants preferably of the phenolic type, synergists, cetane improvers, additives which are incorporated for improving the burner properties of the oil, etc.

Although the alkanol amines of the present invention may be used in conjunction with antioxidants and particularly those of the phenolic type, it is understood that the formation of sediment in storage is different than the oxidative deterioration which may be prevented or retarded by the use of phenolic type compounds. Experiments have shown that certain phenolic type compounds do not retard the formation of sediment in storage, whereas the alkanol amines of the present invention are very effective for this purpose. This will be shown in Example I which is included for comparative purposes and illustrates that compounds which have utility in retarding gum formation in gasoline, for example, actually are of little or no value in retarding sediment formation in burner oil and in many cases actually increase the amount of sediment formed. Similarly, certain known cetane number improvers when added to burner oil increased sediment formation.

In the following examples, the burner oil was subjected to the rays of an arc light for 90 minutes at substantially room temperature. It has been found that this accelerated test correlates with long storage tests as also will be shown in the following examples. The amount of sediment was determined by weighing the precipitate from a hundred milliliters of the burner oil after exposure to the arc light.

EXAMPLE I

The fuel oil used in this example was a commercial #2 fuel oil and comprised a blend of 35% West Texas straight run distillate, 35% of Coastal straight run distillate and 30% of catalytic cycle stock. 0.02% by weight of the additives listed in the following table were added to different samples of the blended burner oil, the samples were then exposed to the arc light for 90 minutes, and the amount of sediment formed was determined by weighing after separation. Prior to exposure to the arc light, the burner oil had a sediment content of .1 mg. per 100 ml. The results are shown in the following table:

Table I

Additive	Sediment, Mg. per 100 ml.
None	7.0
α Naphthol	13.6
Tertiary-butyl catechol	5.4
Pyrogallol	14.5
Phenol	6.3
Nitrobenzene	6.0
Butyl amine	5.0
Dipropylene triamine	14.8
Disalicylal propylene diamine	7.8
2, 2-dinitropropane	18.5
5-amino-4-octanol	1.8

It will be noted from the data in the above table that compounds which are normally effective in reducing gum formation in gasoline were of no substantial value in preventing sediment formation in the burner oil and in fact in most cases increased the amount of sediment. On the other hand, it will be noted that 5-amino-4-octanol retarded sediment formation to a considerable extent.

EXAMPLE II

Another commercial #2 fuel oil comprising a blend of 75% catalytic cycle stock and 25% straight run distillate, was subjected to tests in both the 90 minute arc light treatment and in long time storage. This particular oil was of the type that the components themselves were substantially stable in storage but the blend formed an excessive amount of sediment in storage.

The amount of sediment formation in the components and in the blend with and without exposure to the arc light for 90 minutes is shown in Table II. In addition, results are given on the effect of the addition of 0.01% by weight of 5-amino-4-octanol.

Table II

ACCELERATED TEST

Fuel	Sediment, Mg. per 100 ml.	
	Before arc light	After arc light
Straight Run distillate	0.5	0.5
Catalytic cycle stock	0.4	0.5
Blend of 25% S–R distillate and 75% cat. cycle stock	0.3	2.7
Blend+0.01% 5-amino-4-octanol	0.3	0.0

The results of 96 days' storage tests on different samples of the same fuel oil, with and without additive, are shown in Table III.

Table III

STORAGE TESTS

	Sediment, mg. per 100 ml.			
Days in storage	0	42	67	96
Straight Run distillate	0.5	0.6	1.1	0.5
Catalytic cycle stock	0.4	1.0	1.3	0.7
Blend of 25% S–R Distillate and 75% Catalytic cycle stock	0.3	0.9	2.5	2.8
Blend+0.01% 5-amino-4-octanol	0.3	0.5	0.6	0.3

It will be noted that the straight run distillate and the catalytic cycle stock alone are quite stable in storage and do not form an excessive amount of sediment. However, the blend of straight run distillate and catalytic cycle stock forms 2.7 mg. per 100 ml. of sediment in the accelerated tests and 2.8 mg. of sediment after 96 days in storage. It again will be noted that 5-amino-4-octanol was of high effectiveness in retarding the formation of sediment in the fuel oil. Also, it will be noted that arc light test compares fairly well with the results of 96 days' storage.

EXAMPLE III

In this example another blend of 70% straight run distillate and 30% catalytic cycle stock was subjected to long time storage tests, with and without the addition of 5-amino-4-octanol. An analysis of the blended fuel oil is given in Table IV, and the results of the storage tests are given in Table V.

Table IV

	Blend
A. P. I. gravity, ° Bé.	33.7
I. B. P., ° F.	383
50%	499
90%	581
E. P.	637

Table V

STORAGE TESTS

	Sediment, mg. per 100 ml.												
Days in storage	0	29	35	57	63	127	152	160	190	208	223	236	247
Blend	0	-----	0.7	-----	1.0	1.7	-----	2.2	2.5	-----	2.6	-----	2.8
Blend + 0.02% by wt. of 5-amino-4-octanol	0	0.3	-----	0.3	-----	-----	0.4	-----	-----	0.6	-----	0.5	-----

It will be noted that the fuel oil after 247 days in storage formed 2.8 mg. of sediment per 100 ml. On the other hand, the fuel oil treated with 5-amino-4-octanol formed very little sediment in storage.

These results are shown graphically in Figure I, in which curve A is a plot of the fuel oil without additive and curve B is a plot of the fuel oil containing 0.02% by weight of 5-amino-4-octanol. Figure I graphically illustrates that the addition of 5-amino-4-octanol considerably retards sediment formation in storage.

EXAMPLE IV

This example illustrates the stability of fuel oil insofar as discoloration is concerned. Two different blends of commercial #2 fuel oil were used in these tests. One blend comprised 25% straight run distillate and 75% catalytic cycle stock and the other blend comprised 50% straight run distillate and 50% catalytic cycle stock. The gravity and distillation analysis of the straight run distillate, the catalytic cycle stock and the two blends are given in Table VI.

Table VI

	Straight run distillate	Catalytic cycle stock	Blend of 25% straight run distillate 75% catalytic cycle stock	Blend of 50% straight run-distillate 50% catalytic cycle stock
A. P. I. gravity, ° B6.	39.5	28.9	31.5	34.0
F. B. P., ° F.	376	316	376	374
50%	444	490	474	466
90%	472	544	534	520
E. P.	508	592	580	578

Samples of the above oils were stored, with and without 5-amino-4-octanol, for 43 days and the color determined with a Saybolt Chromometer and with a Union Colorimeter. The oil before storage had an N. P. A. color of less than 1. The results of 43 day storage tests on the components and the blends are given in Table VII.

Table VII

	No additive	With 0.01% of 5-amino-4-octanol
Straight run distillate	+18 Saybolt	+18 Saybolt.
Catalytic cycle stock	about 2 N. P. A.	about 2 N. P. A.
25% straight run distillate, 75% catalytic cycle stock.	----do----	1 N. P. A.
50% straight run distillate, 50% catalytic cycle stock.	about 1½ N. P. A.	about 1 N. P. A.

It will be noted that the blends without additive had colors of about 1½ and 2 N. P. A., whereas the blends containing 5-amino-4-octanol had colors of only 1 N. P. A. Discoloration of fuel oil in storage is important from a commercial aspect because some customers are refusing to accept discolored fuel oils.

EXAMPLE V

The previous examples include the results obtained when using 5-amino-4-octanol as the alkanol amine. The present example shows the results obtained when utilizing other amino alcohols meeting the requirements as hereinbefore set forth.

This example illustrates the stability of the fuel oil insofar as discloration is concerned. The fuel oil used in this example comprised a blend of 25% straight run distillate and 75% catalytic cycle stock. In this example the color stability of the fuel oil samples was determined in a Coleman Universal Spectrophotometer, and Table VIII reports the per cent transmittance at 450 mu after 146 days in storage. The additives were employed in a concentration of 0.01% by weight of the fuel oil.

Table VIII

Additive	Color, Percent Transmittance
None	58
2-amino-2-methyl-3-hexanol	71
2-amino-2-methyl-3-octanol	70
3-amino-4-heptanol	69

It will be noted that the blend without additive had a per cent transmittance of only 58, whereas the blends containing the alkanol amines had a per cent transmittance of 69—71. The higher the per cent transmittance indicates less discoloration and, as seen from the above data, the additives of the present invention serve to considerably retard discoloration of the fuel oil.

EXAMPLE VI

This example reports the results of sediment formation obtained after 315–16 days in storage of the samples described in Example V. These additives were used in a concentration of 0.01% by weight of the blended fuel oil.

Table IX

Additive	Sediment, mg. per 100 ml.
None	14
2-amino-2-methyl-3-hexanol	0.7
2-amino-2-methyl-3-octanol	0.5
3-amino-4-heptanol	1.7

It will be noted that the additives serve to considerably reduce the amount of sediment formed in storage.

We claim as our invention:

1. A blended burner oil containing, as a retardant of sediment formation in storage, from about 0.0005% to about 1% by weight of a primary alkanol amine having an alkyl group of at least 6 carbon atoms in straight chain arrangement and containing not more than 20 carbon atoms per molecule and in which the amino and hydroxyl groups are attached to adjacent carbon atoms.

2. A blended burner oil containing, in a small but sufficient amount to retard sediment formation in storage, a primary alkanol amine having an alkyl group of at least 6 carbon atoms and not more than about 20 carbon atoms per molecule and in which the amino group and the hydroxyl group are attached to adjacent carbon atoms.

3. A blended burner oil containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of a primary amino octanol in which the amino and hydroxyl groups are attached to adjacent carbon atoms.

4. A blended burner oil containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of 5-amino-4-octanol.

5. A blended burner oil containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of a 2-amino-2-alkyl-3-octanol containing not more than 20 carbon atoms per molecule.

6. A blended burner oil containing, as a retardant of

sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of 2-amino-2-methyl-3-octanol.

7. A blended burner oil containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of 1-amino-2-octanol.

8. A blended burner oil containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of a primary amino heptanol in which the amino and hydroxyl groups are attached to adjacent carbon atoms.

9. A blended burner oil containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of 3-amino-4-heptanol.

10. A blended burner oil containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of a primary amino hexanol in which the amino and hydroxyl groups are attached to adjacent carbon atoms.

11. A blended burner oil containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of a 2-amino-2-alkyl-3-hexanol containing not more than 20 carbon atoms per molecule.

12. A blended burner oil containing, as a retardant of sediment formation and discoloration in storage, from about 0.0005% to about 1% by weight of 2-amino-2-methyl-3-hexanol.

13. A blend of straight run petroleum distillate and cracked hydrocarbon oil, both heavier than gasoline, containing, in a small but sufficient amount to retard sediment formation and discoloration in storage, an alkanol amine having an alkyl group of at least 6 carbon atoms and not more than about 20 carbon atoms per molecule and in which the amino group and the hydroxyl group are attached to adjacent carbon atoms.

14. A blend of straight run petroleum distillate and catalytically cracked hydrocarbon oil, both heavier than gasoline, containing a minor amount of 5-amino-4-octanol as a retardant of sediment formation and discoloration in storage.

15. A burner oil heavier than gasoline and normally tending to undergo sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, an alkanol amine having an alkyl group of at least 6 carbon atoms and not more than about 20 carbon atoms per molecule and in which the amino group and the hydroxyl group are attached to adjacent carbon atoms.

16. A burner oil heavier than gasoline and normally tending to undergo sediment formation in storage containing a primary amino octanol in which the amino and hydroxyl groups are attached to adjacent carbon atoms in a small but sufficient amount to retard said sediment formation.

17. A burner oil heavier than gasoline and normally tending to undergo sediment formation in storage containing 5-amino-4-octanol in a small but sufficient amount to retard said sediment formation.

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