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STABILIZED DISTILLATE FUEL OILS AND ADDITIVE COMPOSITIONS THEREFOR

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ABSTRACT OF THE DISCLOSURE

Stabilized petroleum distillate fuel oils containing an effective amount of N,N-dimethylcyclohexylamine and, optionally, an N,N' - di(ortho - hydroxyarylidene) - 1,2-alkylenediamine, for example, N,N'-disalicylidene-1,2-propylenediamine.

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of my copending applications Ser. No. 178,536, filed Mar. 9, 1962, now U.S. Patent 3,186,810, and Ser. No. 291,360, filed June 28, 1963, now abandoned.

This invention relates to stabilized petroleum distillate fuel oils and to additive compositions for stabilizing such fuel oils. More particularly, the invention is concerned with fuel oils, such as diesel engine fuels and burner oils, that are normally susceptible to deterioration with the formation of insoluble sludge and sediment especially at elevated temperatures, which fuel oils have been stabilized to inhibit such deterioration; and to homogeneous liquid concentrates of a combination of additive compounds for so stabilizing such fuel oils, which concentrates are readily soluble in the fuel oils and which are unusually effective to so stabilize such fuel oils.

Resistance to discoloration and formation of insoluble matter is a desirable property in present day fuel oils, including heating oils, diesel fuels and gas turbine fuels, particularly when such fuel oils are subjected to elevated temperatures and oxidizing atmospheres in storage and in use.

Heretofore, a wide variety of additives, including diverse amines, have been suggested as stabilizers for distillate fuel oils. For example, Bonner, in U.S. Patent 2,672,408, discloses oil-soluble amines (including N,N-diethylcyclohexylamine) to be effective to retard color formation in blended oils. In contrast, however, Andress, in U.S. Patent 2,945,749, discloses that, while certain tertiary alkyl primary amines are highly effective in fuel oils to increase color stability and to inhibit sediment formation during storage, "the straight-chained and cycloaliphatic amines not only show no substantial inhibiting effect with respect to formation of sludge sediment, but they actually show an adverse effect in several instances. . . ."

An object of this invention is to improve the stability of petroleum distillate fuel oils against deterioration such as the formation of insoluble sludge, sediment, gum and colored bodies. A specific object is to provide new distillate fuel oil compositions with improved resistance to the formation of colored and insoluble substances at high temperatures and under oxidizing conditions. A further object is to provide additive compositions for distillate hydrocarbon fuel oils, which additive compositions are homogeneous concentrates of a plurality of co-additives and which

concentrates are easily incorporated into said fuel oils and are unusually effective to inhibit discoloration and the formation and deposition of insoluble sludge and sediment in such fuel oils, particularly at high temperatures. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with this invention which comprises a distillate hydrocarbon fuel oil containing

(a) from about 0.00033% to about 0.05% by weight based on the fuel oil of N,N-dimethylcyclohexylamine;

and an additive composition for distillate hydrocarbon fuel oils, which additive composition comprises

(a) from about 85 to about 97 parts by weight of N,N-dimethylcyclohexylamine, and

(b) from about 15 to about 3 parts by weight of an N,N'-di - (ortho - hydroxyarylidene) - 1,2 - alkylenediamine metal deactivator in which the arylidene radical contains 6–7 carbon atoms and the alkylene radical contains 2–3 carbon atoms.

This invention is based on the discovery that N,N-dimethylcyclohexylamine is unusually effective to stabilize fuel oils against deterioration, particularly at elevated temperatures and under oxidizing conditions. The novel fuel compositions show significantly less insoluble residue formation and better color stability than untreated fuels. It is believed that the high degree of stabilization imparted to fuel oils may be attributed to the apparent fact that the N,N-dimethylcyclohexylamine is a uniquely potent antioxidant in these complex hydrocarbon systems at elevated temperatures. In contrast, other amines heretofore suggested in the art, including the corresponding N,N-diethylcyclohexylamine, are much less effective alone for inhibiting oxidative degradation in petroleum distillate fuel oils. Unlike many fuel oil additives proposed heretofore, the N,N-dimethylcyclohexylamine is highly resistant to extraction from the fuel by water, and has no adverse affect on fuel properties in contact with water.

N,N-dimethylcyclohexylamine is well known and conveniently is obtained by methylating aniline with methanol in the presence of an acid catalyst, as described in the art (Kirk-Othmer, Encyclopedia of Chemical Technology, Interscience, vol. 1, pages 915, 916, 923, 924), and catalytically hydrogenating the N-methylated aniline product to the corresponding cyclohexylamine derivative. The technical product, which may often contain small proportions, e.g. 1–5% weight, of the N-monomethylcyclohexylamine, is also suitable for use according to this invention. Such product, as well as the pure dimethyl compound, will be referred to hereinafter as N,N-dimethylcyclohexylamine (DMCHA).

N,N-dimethylcyclohexylamine is normally liquid and readily soluble in the fuel oils. It is substantially not extractable from the fuel oils by water, does not contribute to water hazing or emulsification, and is ashless. Also, it is compatible with other additives normally associated with the finished fuels, such as sludge dispersants, corrosion inhibitors and anti-hazing agents, and may be used to advantage with one or more of such other additives, as more particularly described in my copending application Ser. No. 178,536. In addition to the additive combinations of Ser. No. 178,536, a particularly useful combination according to this invention comprises from about 85% to about 97% by weight of DMCHA and about 15% to about 3% by weight of an N,N'-di-(ortho-

hydroxyarylidene) - 1,2 - alkylenediamine metal deactivator, wherein the arylidene radical contains 6–7 carbon atoms and the alkylene radical contains 2–3 carbon atoms, i.e. 1,2-ethylene and 1,2-propylene. Preferred metal deactivators are N,N'-disalicylidene-1,2-propylenediamine and N,N'-disalicylidene-1,2-ethylenediamine.

N,N-dimethylcyclohexylamine, and its combinations with the above metal deactivators, are normally liquid compositions and may be added as such directly to the fuel oil to be stabilized. Or, if desired, the addition agent may be in the form of a blend, say about 20% to about 80% by weight in a normally liquid inert hydrocarbon carrier solvent, such as kerosene, xylene or the like, i.e. the carrier solvent will be in an amount to constitute from about 20% to about 80% by weight of the composition.

The quantity of N,N-dimethylcyclohexylamine employed in practicing this invention will vary depending on the initial condition and degree of instability of the oil, and the effect desired. While the N,N-dimethylcyclohexylamine may be used in the proportion of about 1 lb. to about 150 lbs. per 1000 barrels of fuel oil (about 0.00033% to about 0.05% by weight based on the fuel), normally from about 1 lb./1000 bbls. (0.00033% wt.) to about 30 lbs./1000 bbls. (0.01% wt.) are used.

Broadly, the distillate fuel oils are mixtures of hydrocarbons boiling in the range of from about 300° F. to about 900° F., which mixtures are normally susceptible to deterioration with the formation of colored bodies and insoluble sludge and sediment under thermal and oxidative conditions. The present invention is particularly concerned with stabilizing such products as diesel engine oils for stationary, marine, automotive and locomotive type engines, said fuels being particularly described by ASTM specification D–975–53T; and domestic and industrial heating oils, as described in ASTM specification D–396–48T. Included are straight run fuel oils, thermally cracked, catalytically cracked, thermally reformed, and catalytically reformed stocks, and blends thereof as known and commonly employed in the art.

In order to more clearly illustrate this invention, preferred modes of practicing it, and the advantageous results to be obtained thereby, the following examples are given in which the amounts and proportions are by weight except where specifically indicated otherwise.

Example 1

N,N-dimethylcyclohexylamine (DMCHA) and N,N-diethylcyclohexylamine (DECHA) are added, in concentrations of 2.5 and 5 lbs. per 1000 barrels, to a typical unstable mid-continent distillate hydrocarbon oil (designated Fuel A), the additions being made to the freshly produced fuel at the refinery. At a second mid-continent refinery, these amines are added at the same concentrations to a blend containing by volume 65% catalytic cracked light cycle oil and 35% straight run No. 1 burner oil (designated Fuel B).

The effectiveness of the amine to inhibit deterioration at elevated temperatures is illustrated by the 300° F. Accelerated Fuel Oil Stability Test (also sometimes referred to as the EMD Diesel Fuel Test, the Union Pacific Test, or the "Nalco" Test). This test is designed to determine the relative stability of distillate fuels under short-term, high temperature, aging conditions involving air exposure. It is also used to evaluate the effectiveness of additives in inhibiting residue formation and color degradation of distillate fuels under the conditions of the test. The proceure consists of aging the fuel sample at 300° F. for 90 minutes, cooling to room temperature, and collecting any insoluble residue by vacuum filtration through a filter paper (blotter). The resultant blotter is compared with a set of standards to obtain a numerical rating of 1 to 20 for the performance of the fuel. The amount and color of the precipitate collected on the blotter determines the rating and indicates the extent of fuel deterioration. The lower the rating the more stable the fuel. In general, a rating of 7 or less is desirable, and 7 may be regarded as the dividing line for purposes of assigning a "pass" (7 or less) or "fail" (greater than 7) rating to the fuel under test. Table 1 compares the effectiveness of these two amines in preventing deterioration at high temperatures as determined by this test.

In addition to the blotter rating, the ASTM color (accoring to ASTM designation: D–1500–58T) of the fuel is also determined before and after aging. Typical results obtained with DMCHA are given in Table 1, together with, for comparison, results for DECHA as additive.

TABLE 1.—N,N-DIMETHYLCYCLOHEXYLAMINE (DMCHA) AND N,N-DIETHYLCYCLOHEXYLAMINE (DECHA)
[Compared in the 300° F. Accelerated Fuel Oil Stability Test]

	Concentration, lbs. 1,000 bbls.	Fuel A		Fuel B	
		ASTM Color	Blotter rating	ASTM color	Blotter rating
Additive:					
None		6.0	17	6.0	18
DMCHA	2.5	L 2.5	5	3.0	11
	5.0	L 2.0	1	2.0	5
DECHA	2.5	3.5	12	L 5.0	17
	5.0	L 3.0	9	L 3.5	12

The above results show that dimethylcyclohexylamine is clearly superior to the prior art diethylcyclohexylamine for stabilizing distillate hydrocarbon oils against deterioration at high temperatures.

Example 2

The effectiveness of DMCHA to inhibit sediment and color formation in five different typical No. 2 fuel oils (A, B, C, G and I) under oxidizing conditions is further illustrated by means of still other methods of evaluation, as described below.

(A) Proposed ASTM Accelerated Stability Test for Distillate Fuel Oil (Appendix 16, 1961 ASTM Standard on Petroleum Products).

The fuel oil under test is aged at 203° F. for 16 hours while oxygen is bubbled through the sample, which is then filtered to remove the insolubles, the amounts of the insolubles determined, and the color of the filtrate measured. Results on fuel oils A, B and C are shown in Table 2–A and are expressed in terms of total insolubles and degree of discoloration produced in the filtered oil under these conditions.

TABLE 2-A.—STABILIZATION OF FUEL OIL AGAINST OXIDATIVE DETERIORATION IN PROPOSED ASTM ACCELERATED STABILITY TEST

DMCHA Conc., lbs./1,000 bbls.	Total insolubles mg./100 ml. fuel oil			Filtrate color, ASTM fuel oil		
	A	B	C	A	B	C
None	5.7	1.3	4.9	5.0	5.0	4.0
5	0.7	0.8	1.1	2.5	5.0	3.0
15	0.6	0.7	0.7	2.5	L 5.0	L 3.0

(B) Great Lakes Pipeline Accelerated Stability Test for No. 2 Fuel Oils.

Samples of the fuel oil are aged 16 hours at 212° F. under 100 p.s.i.g. oxygen in a bomb, then cooled, filtered and the soluble-, insoluble-, and total gum determined. The color of the filtrate is also measured. Two typical No. 2 fuel oils (I and G) were so tested, with and without N,N-dimethylcyclohexylamine (DMCHA) and with both DMCHA and the metal deactivator, N,N'-disalicylidene-1,2-propylenediamine (DMD). The results are shown in Table 2–B.

TABLE 2-B.—RETARDING GUM FORMATION IN THE GREAT LAKES PIPELINE TEST

Additive Conc. lbs./1000 bbls. of No. 2 Fuel Oil		Gum, mg./100 ml.			Color ASTM
DMCHA	DMD	Sol.	Insol.	Total	
[Fuel I]					
		52	27	79	7.0
3		34	16	50	6.5
5		24	14	38	6.5
10		19	8	27	5.0
3	0.5	31	13	44	6.0
5	0.5	24	12	36	5.5
15	0.5	9	3	12	3.5
[Fuel G]					
		31	17	48	6.0
6		13	4	17	4.0
5	0.5	10	2	12	3.5

Tables 2–A and 2–B show that DMCHA, alone or in combination with metal deactivator, is highly effective to inhibit oxidative degradation in fuel oils.

Moreover DMCHA exhibits other characteristics that are highly desirable in additives for fuel oil use. For example, as indicated below, it is substantially not extractable from the fuel oil by water, has no adverse affect on the rate of water settling or on the emulsification tendencies of the fuel, and does not cause troublesome hazing—all of significance since fuel oils are normally stored over water bottoms.

Example 3

Samples of a typical commercial No. 2 fuel oil, with and without DMCHA (7.5 lbs./1000 bbls.), were vigorously shaken for 10 minutes with 10% by volume of tap water. The samples, before and after this water extraction, were evaluated in the 300° F. Accelerated Fuel Oil Stability Test described in Example 1. Fuel oil without DMCHA showed a blotter rating of 17 before and 16 after washing, and ASTM color of L 8.0 and 7.0 before and after washing. Fuel oil containing 7.5 lbs./1000 bbls. of DMCHA showed the same blotter rating of 1 before and after washing, and the same ASTM color rating of L 1.5 before and after washing.

A series of No. 2 fuel oils were treated to contain 20 lbs./1000 bbls. of DMCHA and tested for emulsification and haze tendencies as follows:

In the emulsification test, the oil is agitated violently with 5 volume percent water for 5 minutes in a high speed mixer. If, after standing for 24 hours, no emulsion remains, the procedure is repeated using the same water and fresh oil sample. The number of oil changes that can be made without creating an emulsion is taken as the criterion of performance.

Under these conditions, the fuel oils, with and without DMCHA, performed identically.

In the haze test, the fuel oil plus 0.2 volume percent water is agitated in a high speed mixer for 5 minutes, and the amount of haze produced is determined periodically by withdrawing samples for light transmission measurements.

Under these conditions, the treated and untreated fuels showed substantially identical performance in their rates of recovery to substantially complete light transmission.

Example 4

A commercial No. 2 fuel oil was treated to contain N,N-dimethylcyclohexylamine (DMCHA) or "Primene 81R" (an amine additive understood to consist essentially of C_{12}–C_{14} tertiary alkyl primary amines as disclosed by Andress in U.S. Patent 2,945,749) for purposes of comparison in the quantities tabulated below. The resulting blends were tested for high temperature stability according to the Accelerated Fuel Oil Stability Test described in Example 1. The results are shown in Table 3.

TABLE 3

	Condition of Blotter Appearance and Rating	
	"Primene 81R"	DMCHA
Additive conc., lbs./1,000 bbls.:		
None	Black, 18	Black, 18.
1	do	Grey black, 16.
2	Black, 17	Grey, 11.
3	Grey black, 16	Light grey, 8.
5	do	Tan, 5.
7	Dark grey, 15	Tan. 4,
10	Med. grey, 14	Do.
15		Light tan, 3.

The data show that the cycloaliphatic tertiary amine is clearly superior to the branched chain alkyl primary amine as high temperature stabilizer.

Example 5

N,N-dimethylcyclohexylamine (DMCHA) or other amine as identified below in Table 4 was blended by stirring into a commercial No. 2 fuel oil to provide a concentration of 10 lbs. of amine per 1000 bbls. of oil. The effectiveness of the various amines to inhibit deterioration and insoluble residue formation at elevated temperatures is illustrated by the 210° F. Enjay Test and by the 300° F. Accelerated Fuel Oil Stability Test described in Example 1. The Enjay Test involves a 16 hour exposure of the oil sample at 210° F. and is more fully described by Geller et al. in U.S. Patent 2,912,314 (Example 1) and by Ertelt et al. in U.S. Patent 2,974,025 (Example 2). The results of these tests are shown in Table 4.

TABLE 4.—COMPARISON OF DMCHA WITH OTHER AMINES IN FUEL OIL STABILIZATION

	210° F. Test		300° F. Test	
Additive [1]	ASTM color after test	Mg. residue/ 600 g. fuel oil	Blotter appearance	Rating
None	6—	49.5	Black	18
Aniline	5—	40.8	do	17
N-Me aniline	7—	53.5	do	17
N,N-Me_2 aniline	7—	57.9	do	18
Cyclohexylamine	2½—	6.1	Brown	17
N-Me cyclohexylamine	2—	2.5	Light tan	3
N,N-Me_2 cyclohexylamine (DMCHA)	2—	1.9	do	3
"Primene 81R"	2—	1.3	Grey	8

[1] N-Me stands for N-monomethyl and N,N-Me_2 stands for N,N-dimethyl.

The data show that DMCHA and N-monomethylcyclohexylamine are highly effective to stabilize fuel oil under the conditions of both tests, whereas "Primene 81R" is satisfactorily effective only under the the less stringent thermal conditions of the Enjay test. Further, the effectiveness at the higher temperatures appears attributable to the N-methyl substituents in the mono-and dimethylcyclohexylamines since the parent cyclohexylamine is virtually ineffective in the 300° F. test. This effect of the N-methyl substituents appears to be peculiar to the cyclohexylamine system, since it is absent in the corresponding anilines wherein the N-methyl substituents show the opposite effect of decreasing or destroying the effectiveness of aniline for these purposes.

Example 6

Dimethylcyclohexylamine (DMCHA) and diethylcyclohexylamine (DECHA) are added in equal concentrations to samples of a catalytic cracked light cycle oil, having an API gravity of 60° F. of 28.3 and an ASTM distillation range of 415° to 632° F. immediately as it is produced at a refinery. The treated samples are then blended with straight run No. 1 burner oil having an API gravity at 60° F. of 42.5 and an ASTM distillation range of 345° to 540° F. so as to provide a fuel oil containing 65% cycle oil and 35% burner oil having an API gravity of 60° F. of 33.1 and an ASTM distillation range of 360° to 616° F. The resulting fuels are tested in the 300° F. stability test described in Example 1 and also in the Great Lakes Pipeline Test described in Example 2. Table 5 shows the results.

TABLE 5.—DMCHA COMPARED WITH DECHA AS FUEL OIL STABILIZER

	Concentration lbs./1,000 bbls.	300° F., Stability Test			Great Lakes Pipeline Test					
					Gum, mg./100 ml.			Decrease in Gum Formed, percent		
		ASTM color	Blotter rating	ASTM color	Sol.	Insol.	Total	Sol.	Insol.	Total
Additive:										
None	0.0	D 8	18	L 6.0	31.2	17.2	48.4			
DMCHA	6.0	L 2.5	3	L 4.0	12.6	4.2	16.8	60	76	65
DECHA	6.0	L 3.5	11	L 5.5	31.4	12.1	43.5	−1	30	10

It will be understood that the preceding examples have been given for illustrative purposes solely and that this invention is not limited to the specific embodiments described therein. On the other hand, it will be apparent to those skilled in the art that, subject to the limitations set forth in the general disclosure, many variations and modifications can be made in the materials, proportions and conditions employed, without departing from the spirit or scope of this invention.

From the preceding description, it will be apparent that this invention provides distillate hydrocarbon fuel oils which are stabilized against objectionable deterioration by N,N-dimethylcyclohexylamine and by novel combinations of additives which are unusually effective for such purpose. It will also be apparent that this invention provides novel additive compositions for distillate hydrocarbon fuel oils which compositions are homogeneous concentrates of combination of co-additives which are unusually effective for stabilizing distillate hydrocarbon fuel oils. Accordingly, it will be apparent that this invention constitutes a valuable contribution to and advance in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A distillate hydrocarbon fuel oil containing from about 0.00033% to about 0.05% by weight, based on the fuel oil, of N,N-dimethylcyclohexylamine.

2. A distillate hydrocarbon fuel oil of claim **1** containing from about 0.00033% to about 0.01% by weight, based on the fuel oil, of N,N-dimethylcyclohexylamine.

3. A distillate hydrocarbon fuel oil of claim **1** which also contains from about 3% to about 15% by weight, based on the N,N-dimethylcyclohexylamine, of an N,N'-di(ortho - hydroxyarylidene) - 1,2 - alkylenediamine in which the arylidene radical contains 6–7 carbon atoms and the alkylene radical contains 2–3 carbon atoms.

4. A distillate hydrocarbon fuel oil of claim **2** which also contains from about 3% to about 15% by weight, based on the N,N'-dimethylcyclohexylamine, of an N,N'-di(ortho - hydroxyarylidene) - 1,2 - alkylenediamine in which the arylidene radical contains 6–7 carbon atoms and the alkylene radical contains 2–3 carbon atoms.

5. A distillate hydrocarbon fuel oil of claim **4** in which the N,N' - di(ortho - hydroxyarylidene) - 1,2 - alkylenediamine is N,N' - disalicylidene - 1,2 - propylenediamine.

6. An additive composition for distillate hydrocarbon fuel oils, which comprises

(a) from about 85 to about 97 parts by weight of N,N-dimethylcyclohexylamine, and

(b) from about 15 to about 3 parts by weight of an N,N' - di - (ortho - hydroxyarylidene) - 1,2 - alkylenediamine in which the arylidene radical contains 6–7 carbon atoms and the alkylene radical contains 2–3 carbon atoms.

7. An additive composition of claim **6** which also contains a normally liquid inert hydrocarbon carrier solvent in an amount to constitute from about 20% to about 80% by weight of the composition.

8. An additive composition of claim **6** in which the N,N' - di(ortho - hydroxyarylidene) - 1,2 - alkylene diamine is N,N' - disalicylidene - 1,2 - propylenediamine.

9. An additive composition of claim **8** which also contains a normally liquid inert hydrocarbon carrier solvent in an amount to constitute from about 20% to about 80% by weight of the composition.

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Disclaimer

3,490,882.—*William P. Dunworth*, Wilmington, Del. STABILIZED DISTILLATE FUEL OILS AND ADDITIVE COMPOSITIONS THEREFOR. Patent dated Jan. 20, 1970. Disclaimer filed Sept. 17, 1976, by the assignee, *E. I. du Pont de Nemours and Company*.

The term of this patent subsequent to June 1, 1982, has been disclaimed. [*Official Gazette November 23, 1976.*]