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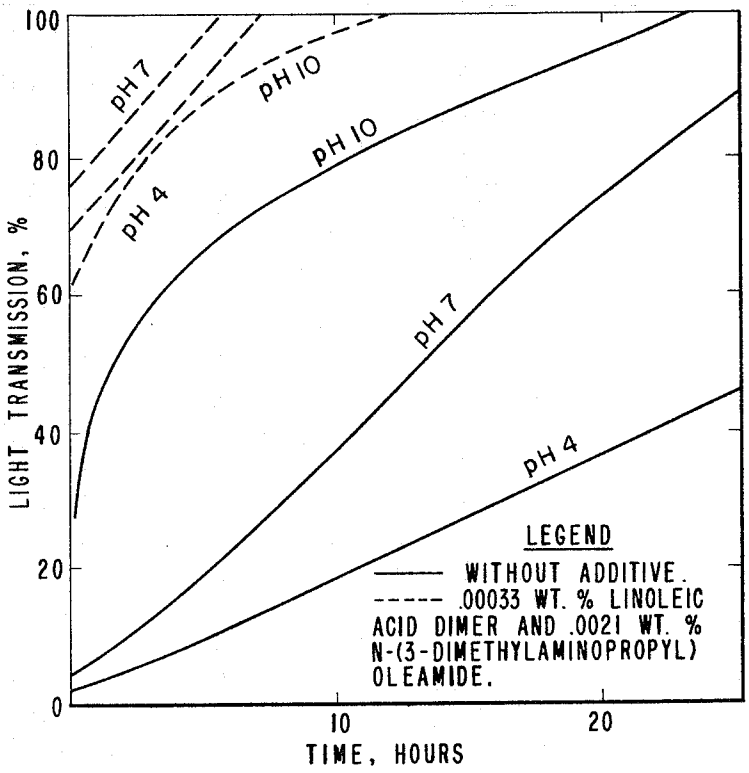

INVENTOR
HARRY D. MARVEL, JR

BY Francis J. Crowley

ATTORNEY

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STABILIZED FUEL OIL COMPOSITIONS

Harry D. Marvel, Jr., Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention relates to stabilized petroleum distillate fuels. It also relates to stabilizer compositions for such fuels.

Petroleum distillate fuels are susceptible to deterioration during transportation and storage. This deterioration manifests itself in a number of ways. Fuels which are clear and colorless at the refinery may appear hazy or discolored after relatively short periods of time in pipeline systems and storage tanks. Another and even more undesirable result is the formation of insoluble sludge which clogs filters, screens, and other small orifices in diesel engine and fuel burner systems. A contributing factor to such problems is the small amount of water which inevitably finds its way into the fuel during the time it is being transported and stored.

The present invention pertains to petroleum distillate fuels containing a combination of chemical additives which have shown an unexpected and unusual ability to prevent haze, color degradation, sludge formation, filter plugging, emulsification and rusting of storage containers. More specifically, this invention provides a stabilized fuel composition comprising a petroleum distillate fuel oil and about 0.001 to 0.02 percent by weight, based on weight of the fuel oil, of a mixture of a linoleic acid dimer and N-(3 - dimethylaminopropyl) oleamide in a respective weight ratio of 1:1 to 1:20. In a further embodiment of this invention, it has been found that the 1:1 to 1:20 mixture of linoleic acid dimer and N-(3 - dimethylaminopropyl) oleamide may be prepared as a concentrate in 20 to 80% by weight of fuel oil. Such a concentrate is a convenient means for handling the additive mixture of this invention, and such a concentrate mixes readily with fuel oils that are to be stabilized.

The attached drawing is presented to illustrate that the additive compound of this invention assists in the separation of water from fuel oils. This drawing is discussed in detail in Example V.

The linoleic acid dimer used in this invention is a commercially available material. The preparation of such a dimer is described in U.S. Patent 2,482,761 and in an article by Charles G. Goebel, Journal of the American Oil Chemists Society, vol. 24, pp. 65–8 (1947). Since commercial linoleic acid may contain small amounts of other fatty acids, dimers of these acids may also be present in the product used in this invention. It is also well known in the art that such a product may contain small amounts of trimer acids and also minor amounts of unreacted acids. Commercial linoleic acid dimers which contain these other materials are suitable for use in this invention.

The N-(3-dimethylaminopropyl) oleamide can be prepared by heating equimolar amounts of oleic acid and 3-dimethylaminopropylamine at a temperature in the range of 150°–200° C. until reaction is substantially complete, as shown by the formation and separation of an essentially stoichiometric amount of water. If desired, an entrainment solvent with a suitable boiling temperature can be used to facilitate the removal of the water formed by the reaction. Such a solvent, if used, can be left in the product or separated from it by distillation, as is convenient.

The stabilizer combination of this invention is useful in petroleum distillate fuels which are essentially mixtures of hydrocarbons boiling in the range of 300° to 900° F. The present invention is particularly concerned with stabilizing such products as fuel oils for stationary, marine,

automotive, and locomotive type diesel engines, said fuels being particularly described in ASTM Specification D975–60T, and fuel oils for domestic and industrial heating, as described in ASTM Specification D396–62T. Included are straight-run fuels, thermally cracked, catalytically cracked, thermally reformed, and catalytically reformed stocks, and blends thereof, as commonly employed in the art.

The preferred total concentration of the combinations of additives of this invention is about 0.002 to about 0.02 percent by weight and the preferred ratio of dimer acid to oleic acid amide is from about 1 to 2 to about 1 to 10. A narrower range which is more preferred from a cost standpoint is a total concentration of about 0.003 to about 0.007 percent and a ratio of linoleic acid dimer to oleic acid amide of about 1 to 5 to about 1 to 7. If desired, other additives may be used along with the stabilizer combination of this invention. It has been found that a metal deactivator such as N,N'-disalicylidene-1,2 - propanediamine, in an amount of 0.00003 to 0.0015% based on the weight of the fuel oil, works well with the additives of this invention.

Linoleic acid dimer has been disclosed in U.S. Patent 2,632,695 as a rust inhibitor for light petroleum products. However, it is quite surprising to discover that this dimer is capable of enhancing the stabilizing properties of an oleic acid amide. Furthermore, the rust-inhibitive properties of the amide appear to be retained in the presence of the N-(3 - dimethylaminopropyl) oleamide. This again is somewhat unexpected in view of the fact that the amide contains what might be considered a basic functional group; that is, the tertiary amino group; whereas the dimer contains acidic groups. Amides of the type used in this invention have been previously disclosed as additives for fuel oils in U.S. Patent 2,805,135.

For a clearer understanding of the invention, the following specific examples are given. These examples are intended to be merely illustrative of the invention and not in limitation thereof. Unless otherwise specified, all parts are by weight.

Example I

A mixture of N-(3-dimethylaminopropyl) oleamide and a linoleic acid dimer was stirred into a No. 2 petroleum distillate fuel oil in the proportions shown in Table 1. The linoleic acid dimer used in all of the examples had a neutralization equivalent of 290–300; an iodine value of 80–95; an acid value of 180–192; and a saponification value of 185–195. Its dimer content was approximately 85%; its trimer content was approximately 12%; and it had a monomer content of approximately 3%. To test the effectiveness of this mixture in preventing the clogging of filter screens in oil burners, a standard test devised for this purpose was carried out. This test consists of contaminating 4 liters of the fuel that is to be tested with 30 grams of a synthetic sludge composed of 5% lampblack, 52.5% distilled water, and 42.5% of the base fuel to be tested. The synthetic sludge is prepared by blending the fuel oil and the water together in a high-speed agitator while gradually adding the lampblack. The mixture is blended until a smooth homogeneous paste is obtained. The sludge-containing fuel is circulated for two hours through a Sundstrand fuel unit which contains a screen on the inlet side of the pump. The screen, which is standard equipment with the Sundstrand Model J3BA fuel unit, was in the form of a cup 2¼ inches in diameter and 2¼ inches deep. The screen was 90 x 100 mesh, made from 0.0045 inch diameter "Monel" wire, with openings of approximately 150 x 170 microns. The quantity of material adhering to the screen at the end of two hours was determined by washing into a filter crucible, freeing of oil, and drying. Tests were made with and

without additives. When a fuel oil which contained the synthetic sludge but no chemical additive was circulated through the system for two hours, there was obtained a residue of 615 mg. from the filter screen. When the same petroleum distillate containing additives was circulated through the system for the same period of time, there was a reduction in the amount of residue upon the screen, and this reduction is reported in Table 1.

Example II

A concentrated mixture suitable for use as a fuel oil addition agent was prepared by mixing 6.5 parts of N-(3-dimethylaminopropyl) oleamide and 1.0 part of linoleic acid dimer in 7.5 parts kerosene. This additive concentrate was mixed with No. 2 fuel oil in various amounts to give the total active ingredient concentrations specified

TABLE 1

	Additive, Weight Percent			Ratio of Amide to Acid	Percent Reduction in Screen Residue
	N-(3-dimethylaminopropyl) oleamide	Linoleic Acid Dimer	Combined Total		
Control #1	0.0016	None	0.0016		45
Control #2	None	0.0016	0.0016		28
Control #3	None	0.00022	0.00022		17
Test A	0.0014	0.00022	0.0016	6.5	66
Test B	0.0009	0.0007	0.0016	1.3	65
Test C	0.00156	0.00077	0.0023	20	69
Test D	0.017	0.003	0.02	5.7	82

in Table 2. These fuel oil mixtures were evaluated in the tests described in Example I except that oil samples of one gallon containing 15 grams of the synthetic sludges composed of 10% lampblack, 50% water, and 40% of the base fuels were used. The results listed in Table 2 show that the combination of additives of this invention is effective in dispersing sludges and sediments in a variety of fuel oils containing straight-run stocks, fluid catalytically cracked stocks, thermally cracked stocks, and mixtures of such stocks, all of these being products which are conventionaly produced in the manufacture of distillate fuel oils.

TABLE 2

	Composition of Fuel Oil, by Volume					
Fuel Number	1	2	3	4	5	6
Fluid catalytic cracked		100%	100%		81.5%	70%
Thermal cracked	100%			100%		
Straight run					18.5%	30%
Additive Concentration, Percent by Weight:	Reduction in Screen Residue					
0.00125		74%		88%		
0.0025		80%		90%	75%	96%
0.005	78%	90%	91%			

Example III

An additive concentrate of the same composition as that used in Example II was added to a group of fuel oils of different types to give a total active ingredient concentration in separate samples of 0.0025 and 0.005 percent by weight. The oils were stored in vented glass bottles for 12 weeks at 110° F., and then they were filtered through fritted glass discs. The discs were then washed free of oil and dried to determine the amounts of insoluble residue formed. The results listed in Table 3 show that the proposed combination of additives is effective in increasing the stability of a variety of fuel oils, as shown by decreases in insoluble residue. It is generally recognized by those familiar with petroleum stabilization that one week of storage at 110° F. under the conditions of this procedure is equivalent to approximately one month under the conditions normally existing during the storage and distribution of fuel oils. In Table 3,

Fuels No. 5 and 6 are the same as the correspondingly numbered fuels in Example II.

TABLE 3

Fuel Number	Additive Concentration, Percent by Weight	Insoluble Residue, mg./100 ml.
5	None	3.8
	0.0025	2.9
	0.005	2.4
6	None	2.1
	0.0025	0.4
	0.005	0.2
7 [1]	None	12.2
	0.0025	2.1
	0.005	1.9

[1] Fuel No. 7 was a commercial No. 2 fuel oil blend.

Example IV

A mixture of 6.5 parts N-(3-dimethylaminopropyl) oleamide, 1.0 part of linoleic acid dimer, and 7.5 parts of kerosene was added to four of the No. 2 fuel oils described in Examples II and III. The total concentration of active ingredients in these oils was 0.005 weight percent (0.000665%) linoleic acid dimer, 0.004335% N-(3-dimethylaminopropyl) oleamide. 700 milliliters of each of the oils were stored in vented glass bottles at 210° F. for 16 hours. The oils were then filtered through medium porosity sintered glass crucibles and the crucibles were washed free of oil and dried to determine the amount of insoluble residue formed. The ASTM Union color of the filtrate was also determined by ASTM Method D155. Fuel oils which form more than 7 mg. of sludge in this test are expected to clog filters in normal use. The results listed in Table 4 show that the combinations of additives of this invention are effective in reducing oil deterioration and color formation under the relatively severe conditions of temperature and time involved in this procedure.

TABLE 4

Fuel Number	Insoluble Residue		ASTM Union Color	
	Without Additive	With Additive	Without Additive	With Additive
1	11.5	1.0	6	2
2	31.2	0.2	3½	2
3	9.2	0.8	7	1½
4	35.0	1.1	7	1½

Example V

The effectiveness of the combination of additives of this invention in assisting the separation of fuel oils and water with which the former may become mixed was demonstrated in tests in which No. 2 fuel oil was mixed with 0.2% water by agitation in a milkshake mixer for five minutes and then allowed to stand. Small samples of the fuel were withdrawn periodically for measurements of light transmission with a photoelectric colorimeter. The percent light transmission v. time is plotted in the attached drawing, and it shows that the additive combination of

this invention greatly speeds up the separation of suspended water, whether the water is acidic (pH 4), neutral (pH 7), or alkaline (pH 10).

Example VI

An additive concentrate composed of 6.5 parts of N-(3-dimethylaminopropyl) oleamide, 1.0 part of linoleic acid dimer, and 7.5 parts of kerosene was added to 8 different samples of No. 2 fuel oil in an amount sufficient to give each sample a total active ingredient concentration of 0.005% by weight. Each fuel oil was agitated violently with 5% water for 5 minutes in a high speed milkshake mixer and then allowed to settle for 24 hours. Since there was no evidence of an emulsion after standing for 24 hours, the water layer was separated and mixed with another portion of the fuel oil. This procedure was repeated until each water layer had been mixed with 5 different portions of one of the fuel oil samples containing the linoleic acid dimer and the oleamide. There was no evidence of emulsion in any of the water layers. In the same test, these same fuel oils without the additive combination of this invention formed stable emulsions after 4 or fewer changes of the oil layer.

Example VII

An additive concentrate composed of 6.5 parts of N-(3-dimethylaminopropyl) oleamide, 1.0 part of linoleic acid dimer, and 7.5 parts of kerosene was added to samples of two different fuel oils in an amount sufficient to give the total additive concentrations shown in Table 5. One of the fuel oils used in this test was 100% fluid catalytically cracked No. 2 fuel oil which is referred to in Table 5 as "Fuel 8" and the other sample was a commercial blend of catalytically cracked, thermally cracked, and straight run components. The effectiveness of the additive combination of this invention was evaluated by ASTM Method D665–54 in which water and the fuel oils containing the additive combination of this invention were stirred for 24 hours at 140° F. in contact with polished SAE 1020 steel test pieces. At the end of this period, the specimens were examined. The amount of surface rusted was observed and the results are reported in Table 5.

TABLE 5

Additive Concentration, Percent by Weight	Percent of Specimen Surface Rusted	
	Fuel 8	Fuel 9
None	100	100
0.0006	90	15
0.0012	Trace	5
0.0025	Trace	Trace
0.005	Nil	Nil

Example VIII

The present example illustrates the beneficial effect of N,N'-disalicylidene-1,2-propanediamine when used in conjunction with linoleic acid dimer and N-(3-dimethylaminopropyl) oleamide. A stabilizer concentrate containing 6.5 parts of N-(3-dimethylaminopropyl) oleamide and 1.0 part of linoleic acid dimer in 7.5 parts of kerosene was added to a No. 2 catalytically cracked fuel oil in an amount sufficient to give a total concentration of dimer and oleamide of 0.01% by weight. To a separate portion of the fuel containing the dimer and oleamide there was also added 0.00067% by weight of N,N'-disalicylidene-1,2-propanediamine. These fuels, along with the same fuel containing no additives whatsoever and a fuel containing only 0.00067% by weight of N,N'-disalicylidene-1,2-propanediamine, were stored for 12 weeks at 110° F. in vented glass bottles. At the end of this period, the fuels were filtered and the amount of insoluble residue was determined. The ASTM Union colors of the filtrates were also determined by ASTM Method D155. The results reported in Table 6 showed a beneficial effect which is obtained by using N,N'-disalicylidene-1,2-propanediamine in conjunction with the combination of linoleic acid dimer and N-(3-dimethylaminopropyl) oleamide.

TABLE 6

Additive Concentrations, Percent by Weight		Insoluble Residue, mg./100 ml.	ASTM Union Color
Mixture of 13.3% Linoleic Acid Dimer and 86.7% N-(3-dimethylaminopropyl) Oleamide	N, N'-disalicylidene-1, 2-propanediamine		
None	None	12.5	6–
None	0.00067	12.4	6–
0.01	None	4.5	5–
0.01	0.00067	2.8	5–

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

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

1. A fuel oil composition comprising a petroleum distillate fuel oil and a minor amount of a mixture of linoleic acid dimer and N-(3-dimethylaminopropyl) oleamide sufficient to stabilize said fuel oil against deterioration, said dimer and said oleamide being present in the mixture in a respective weight ratio of about 1:1 to about 1:20.

2. A fuel oil composition comprising a petroleum distillate fuel oil and about 0.001% to about 0.02% by weight based on the weight of the fuel oil of a mixture of a linoleic acid dimer and N-(3-dimethylaminopropyl) oleamide in a respective weight ratio of about 1:1 to about 1:20.

3. The composition of claim **2** in which the mixture is present in an amount of about 0.002% to about 0.02% by weight and the ratio of linoleic acid dimer to N-(3-dimethylaminopropyl) oleamide is about 1:2 to about 1:10.

4. A stabilizer additive for fuel oils comprising a mixture of linoleic acid dimer and N-(3-dimethylaminopropyl) oleamide in a respective weight ratio of about 1:1 to about 1:20, the balance being essentially a petroleum distillate fuel oil in an amount of 20–80% by weight of the stabilizer additive.

5. A fuel oil composition comprising a petroleum distillate fuel oil and about 0.001 to about 0.02% by weight based on the weight of the fuel oil of a mixture of a linoleic acid dimer, N-(3-dimethylaminopropyl) oleamide in a respective weight ratio of about 1:1 to about 1:20, and 0.00003 to 0.0015% by weight based on the weight of the fuel oil of N,N'-disalicylidene-1,2-propanediamine.

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DANIEL E. WYMAN, *Primary Examiner.*

W. J. SHINE, *Assistant Examiner.*