United States Patent Office

2,701,187

Patented Feb. 1, 1955

2,701,187

COLOR STABILIZATION IN FUEL OILS

Harry J. Andress, Jr., Pitman, N. J., assignor to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

No Drawing. Application July 16, 1952, Serial No. 299,248

6 Claims. (Cl. 44—63)

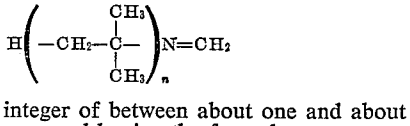
This invention relates to the improvement of non-lubricating petroleum fractions. It is more particularly concerned with No. 2 fuel oils containing additives adapted to improve color characteristics and to inhibit the appearance of sediment during prolonged storage periods.

Fuel oils, particularly No. 2 fuel oils, are prone to develop undesirable color and to form sediment during prolonged storage periods. Such undesirable properties have an adverse effect on burner operation and, also, lead to increased customer resistance. The effect of the development of color on fuel oil properties is not readily explainable. It can be postulated that color development hastens degradation of the oil. In any event, regardless of the physical effects color may have, it is the general experience in the field that customers refuse to purchase highly-colored fuel oils, as those skilled in the art will readily understand. As is well known to those familiar with the art, many additives have been proposed to inhibit the formation of sediment in fuel oils. Many of these additives, however, fail to improve the color of the fuel oil, and often degrade the color. Accordingly, resort has been had to other additives, in addition to the sedimentation stabilizer, for the purpose of improving the color stability.

It has now been found that increased color stability and the inhibition of sedimentation can both be achieved by the addition of a single additive to a fuel oil. It has been discovered that condensation products of formaldehyde with specific aliphatic amines, when added to a fuel oil in small amounts, effectively inhibit the formation of color and of sediment during storage.

Accordingly, it is object of this invention to provide a fuel oil having improved color stability and resistance to sedimentation. Another object is to provide a method of inhibiting the formation of color and of sediment in fuel oils during storage. A specific object is to provide distillate fuel oils containing minor amounts of the reaction product of formaldehyde with certain aliphatic amines. A more specific object is to provide distillate fuel oils, of the No. 2 fuel oil type, containing minor amounts of the reaction product of formaldehyde with a branched-chain alkyl primary amine having a tertiary carbon atom attached to the nitrogen atom thereof or with a normal aliphatic primary monoamine, in order to increase the color stability and the resistance to sedimentation of the fuel oil. Other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description.

Broadly stated, the present invention provides a distillate fuel oil containing between about 10 pounds and about 200 pounds per thousand barrels, of an additive selected from the group consisting of (1) a compound having the formula,



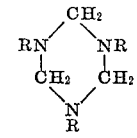
wherein n is an integer of between about one and about six, and (2) a compound having the formula,

$$(RN{=}CH_2)_3$$

wherein R is a normal aliphatic monovalent hydrocarbon radical containing between about 8 carbon atoms and about 18 carbon atoms per radical.

The additives contemplated herein are certain formaldimines produced by the condensation of an amine

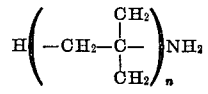
with formaldehyde. In general, the reaction involved produces a compound having the formula, $RN{=}CH_2$. The normal aliphatic primary amines, however, do not form stable monomers. The monomers quickly trimerize under the conditions of the condensation reaction to form compounds of the formula, $(RN{=}CH_2)_3$, and having the structural formula,



On the other hand, the primary alkylamines having a tertiary carbon atom attached to the nitrogen atom thereof do not undergo the trimerization reaction. They are unique in that they form stable, distillable monomeric formaldimines.

The amines which produce the trimeric formaldimines contemplated herein are the normal, aliphatic monoamines having between about 8 carbon atoms and about 18 carbon atoms per molecule. These amines can be saturated or unsaturated. Likewise, mixtures of these amines, as well as relatively pure amines, can be used to produce the formaldimines. Non-limiting examples of normal aliphatic amines utilizable herein are n-octylamine, n-octenylamine, n-decylamine, n-undecylamine, n-dodecenylamine, n-dodecadienylamine, n-tetradecylamine, n-pentadecylamine, n-hexadecylamine, n-hexadecenylamine, n-octadecylamine, n-octadecenylamine, and n-octadecadienylamine.

The alkylamines which form the monomeric formaldimines contemplated herein are those having a tertiary carbon atom attached to the nitrogen atom thereof. These alkylamines have an alkyl chain composed of one or more recurring tertiary butyl groups. The general formula thereof is



wherein n is an integer of one or more, preferably between one and about six. Mixtures of two or more alkylamines of the type described herein can be used to produce mixtures of formaldimines which are utilizable in accordance with this invention. Non-limiting examples of the alkylamines are 1,1,3,3,-tetramethylbutylamine; 1,1,3,3,-5,5-hexamethylhexylamine; 1,1,3,3,5,5,7,7-octamethyloctylamine; 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyldodecylamine; and mixtures of the foregoing. These amines are commercially available in relatively pure form and in mixtures containing two or more alkylamines.

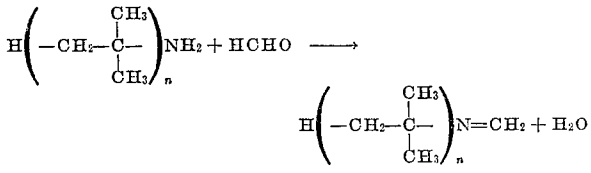
Formaldehyde is the only aldehyde found utilizable to produce condensation products which improve the color characteristics of fuel oils. It was found that the additives tested which were made from other aldehydes either failed to improve the color or in some instances produced a greater amount of color than was produced by the uninhibited fuel oil. All of the usual forms of formaldehyde are utilizable and contemplated for producing the formaldimines utilizable in this invention i. e., aqueous solutions (formalin), paraformaldehyde, trioxymethylene, etc.

The formaldimines contemplated herein are prepared by reacting the amine and the aldehyde, in a 1:1 molar proportion using any of the methods well known to those skilled in the art. Ordinarily, in the initial stages, the reaction is exothermic. In order to complete the reaction, the water formed therein should be removed. This can be accomplished, for example, by heating the reaction mixture to a temperature above the boiling point of water, or by removing the water by azeotropic distillation with a non-polar solvent, such as benzene or toluene. It must be strictly understood that this invention is not limited by the method for producing the formaldimine. The additives have been prepared by several methods, and each method has produced formaldimines in accordance with the following equations:

(1) With normal aliphatic amines:

$$3RHN_2+3HCHO\rightarrow(RN=CH_2)_3+3H_2O$$

(2) With the aforedescribed alkylamines:



As mentioned hereinbefore, the formaldimines produced in accordance with Equation 2 are stable, distillable liquids. Accordingly, they can be further purified by distillation means. In practice, however, the formaldimines as formed according to the equations set forth hereinbefore are sufficiently pure for the purposes of this invention without resorting to further purification.

The fuel oils which are improved in accordance with this invention are hydrocarbon fractions having an initial boiling point of at least about 300° F. and an end point not higher than about 750° F., and boiling substantially continuously throughout their distillation range. Such fuel oils are generally known as distillate fuel oils. It must be strictly understood, however, that this term is not restricted to straight-run distillate fractions. As is well known to those skilled in the art, the distillate fuel oils can be straight-run distillate fuel oils, catalytically or thermally cracked distillate fuel oils, or mixtures of straight-run distillate fuel oils, naphthas and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well known commercial methods, such as, acid or caustic treatment, solvent refining, clay treatment, etc.

The distillate fuel oils are characterized by their relatively low viscosities, pour points, and the like. The principal property which characterizes the contemplated hydrocarbons, however, is the distillation range. As mentioned hereinbefore, this range will lie between about 300° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower range falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially continuously throughout its distillation range.

Especially preferred among the fuel oils contemplated herein are Nos. 1, 2 and 3 fuel oils used in domestic heating and as diesel fuel oils. The domestic fuel oils generally conform to the specifications set forth in ASTM Specifications D396–48T. Specifications for diesel fuels are defined in ASTM Specifications D975–48T. Such fuel oils have a tendency to form sediment, sludge, and color during storage.

In order to inhibit effectively the formation of sediment or sludge, and the development of color in fuel oils, the formaldimines defined herein are added thereto in concentrations varying between about 10 pounds per thousand barrels of oil and about 200 pounds per thousand barrels of oil. Preferably the concentration varies between about 25 and about 200 pounds per thousand barrels. In terms of weight per cent, based on the weight of the fuel oil, the concentrations vary, preferably, between about 0.01 per cent and about 0.1 per cent.

If it is desired, the fuel oil compositions of this invention can contain other additives for the purpose of achieving other results. Thus, for example, there can be present foam inhibitors, antirust agents, and ignition and burning quality improvers. Examples of such additives are silicones, dinitropropane, amyl nitrate, metal sulfonates, and the like.

The following specific examples are for the purpose of illustrating the fuel oil compositions of this invention, and of exemplifying the specific nature thereof. It is to be strictly understood, however, that this invention is not to be limited by the particular additives and fuel oils, or to the operations and manipulations described therein. Other formaldimines and fuel oils, as discussed hereinbefore, are utilizable, as those skilled in the art will readily appreciate.

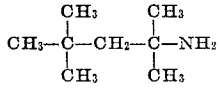
The tests used to determine the sedimentation characteristics of the fuel oils are the 110° F. storage test and the 80° F. storage test. In the 110° F. storage test, a 500-milliliter sample of the fuel oil under test is placed in a convected oven maintained at 110° F., for a period of six weeks. Then, the sample is removed from the oven and cooled. The cooled sample is filtered through a tared asbestos filter (Gooch crucible) to remove the insoluble matter. The weight of such matter, in milligrams, is reported as the amount of sediment. The 80° F. storage test is conducted in a similar manner, with the exceptions that a temperature of 80° F. is used and that the test is run for a period of one month. In both tests, a sample of the blank, uninhibited oil is run along with the fuel oil blend under test. The effectiveness of a fuel oil composition containing an inhibitor is determined by comparing the test data therefor with the test data for the uninhibited, blank fuel oil.

The color characteristics of a fuel oil are determined by means of the percentage of light transmision of the oil after it is subjected to the storage tests. The determination of light transmision involves the photoelectric measurement of light transmision as determined by a Lumetron Colorimeter.

Three different fuel oils have been used for the purpose of demonstrating the present invention. Fuel oil A is a blend of 70 per cent distillate stock derived from continuous catalytic cracking and 30 per cent air-caustic sweetened straight-run distillate stock. It has a boiling range of between about 320° F. and about 640° F. Fuel oil B is a blend of 85 per cent catalytically cracked stock and 15 per cent straight-run stock, which boils between about 325° F. and about 650° F. Fuel oil C is similar to fuel oil A, except that it contains about 75 per cent cracked stock and 25 per cent straight-run distillate stock. These fuels are typical domestic No. 2 fuel oils.

FORMALDIMINES OF TERTIARY ALKYLAMINES

The tertiary alkylamines used to produce the formaldimines set forth in the examples are commercially available compounds produced by Rohm and Haas Company, Washington Square, Philadelphia 5, Pennsylvania. Tertiary octylamine has the structural formula,



Alkylamine 81 is a mixture of primary amines having the same type of tertiary alkyl structure as the tertiary octylamine. The number of carbon atoms in the compounds in this mixture ranges from about twelve to about fifteen. Alkaylamine JM is a similar mixture of tertiary alkylamines as in Alkylamine 81, but having an average of about eighteen to twenty-four carbon atoms. Typical properties of these amines are set forth in Table I.

Table 1

	t-octyl-amine	Alkyl-amine 81	Alkyl-amine JM
Boiling Range, °C	140 at 760 mm.	100–150 at 10 mm.	124–192 at 15 mm.
Specific Gravity (25° C.)	0.771	0.819	0.823.
Refractive Index, n_D^{25}	1.4213	1.4455	1.457.
Neutral Equivalent	131	208	286.
Flash Point, ° F	92	196	260.

EXAMPLE 1

The following preparation illustrates a typical method for producing the formaldimines utilizable in this invention. One mole (200 grams) of Alkylamine 81 was stirred with one mole (30 grams) of trioxymethylene. The mixture was slowly heated to about 150° C. and maintained at that temperature, until one mole of water had been collected (about three hours). The final product was a yellow-orange liquid having an unpleasant odor characteristic of formaldimines. This monomeric formaldimine was blended in portions of fuel oils A and B at various concentrations. The resultant blends were subjected to the 80° F. and the 110° F. storage tests. Pertinent data are set forth in Table II.

EXAMPLE 2

A monomeric formaldimine was produced from tertiary butylamine and formaldehyde. This compound was tested in fuel oil B at various concentrations, with the results shown in Table II.

EXAMPLE 3

A monomeric formaldimine was prepared from the aforedescribed tertiary octylamine and formaldehyde. This compound was tested in fuel oil B, at various concentrations, in the 80° F. and the the 110° F. storage tests. Pertinent data therefor are set forth in Table II.

EXAMPLE 4

A monomeric formaldimine produced from Alkylamine JM and formaldehyde was blended in fuel oil A. This blend was subjected to the 80° F. and the 110° F. storage tests. Pertinent data are set forth in Table II.

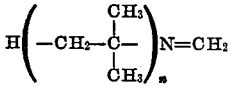
EXAMPLES 5 THROUGH 10

Monomeric formaldimines of various aldehydes and Alkylamine JM were blended in portions of fuel oil A. These blends, when subjected to the 80° F. and the 110° F. storage tests, showed the results for which data are set forth in Table II.

Table II

Example	Formaldimine of—		Fuel Oil	Concn., lbs./1,000 bbl.	110° F. Storage Test—6 weeks		80° F. Storage Test—1 month
	Amine	Aldehyde			Sediment, mg./liter	Transmission, Percent	Transmission, Percent
1	Alkylamine 81	Formaldehyde	B	10	9	65.6	84.0
	do	do	B	25	3	72.3	85.3
	do	do	B	50	13	71.7	85.5
	(Blank)		B		46.4	57.8	74.4
	Alkylamine 81	Formaldehyde	A	200	5.2	26.8	45.5
	(Blank)		A		107.4	3.0	7.2
2	t-butylamine	Formaldehyde	B	10	23	46.2	79.0
	do	do	B	25	19	52.4	81.3
	do	do	B	50	12	60.4	80.0
	(Blank)		B		54.4	40.5	65.8
3	t-octylamine	Formaldehyde	B	10	21	45.2	80.4
	do	do	B	25	5	65.4	82.4
	do	do	B	50	9	60.1	82.4
	(Blank)		B		58	35.1	66.8
4	Alkylamine JM	Formaldehyde	A	200	4.6	24.3	43.6
5	do	Acetaldehyde	A	200	62	3.6	9.2
6	do	Butyraldehyde	A	200	38	3.2	2.0
7	do	Benzaldehyde	A	200	40	3.0	18.0
8	do	Furfural	A	200	42	3.5	6.8
9	do	Glyoxal	A	200	29	4.0	1.2
10	do	Salicylaldehyde	A	200	62	5.6	18.0
	(Blank-4-10)		A		107.4	3.0	7.2

It will be apparent from the foregoing examples that formaldimines having the structural formula,



wherein n is an integer of between one and about six, vastly improve the color characteristics of fuel oils and, also, effectively inhibit sedimentation. As demonstrated

in Examples 5 through 10, formaldimines made from other aldehydes do not possess such a combination of valuable properties.

FORMALDIMINES OF NORMAL ALIPHATIC AMINES

The normal aliphatic amines utilized herein to prepare formaldimines were those sold by Armour and Company, Chicago, Illinois. They are known by the trade name "Armeen." Armeen C is derived from coconut oil, Armeen T from tallow, and Armeen S from soy bean oil. These amines are mixtures of primary aliphatic normal amines having the weight percentage compositions shown in Table III. Other properties of these amines can be derived from the brochures on the subject published by Armour and Co.

Table III

Normal Amine	Armeen T	Armeen S	Armeen C
Octyl			8
Decyl			9
Dodecyl			47
Tetradecyl			18
Hexadecyl	30	10	5
Octadecyl	25	10	5
Octadecenyl	45	35	8
Octadecadienyl		45	

Table IV

Example	Amine	Aldehyde	Fuel Oil	Concn., lbs./1,000 bbl.	110° F. Storage Test—6 weeks		80° F. Storage Test—1 month
					Sediment, mg./liter	Transmission, Percent	Transmission, Percent
11	Armeen T	Formaldehyde	B	10	17	64.5	89.3
	do	do	B	25	7	66.5	89.3
	do	do	B	50	6	71.1	90.4
	(Blank)		B		51	68.0	88.6
	Armeen T	Formaldehyde	C	25	25	22.3	48.2
	do	do	C	50	15	26.2	60.0
	do	do	C	100	15	31.0	63.4
	(Blank)		C		52	19.2	47.1
12	Armeen S	Formaldehyde	B	10	31	34.2	57.5
	do	do	B	25	10	38.0	59.0
	do	do	B	50	7	44.7	60.2
	(Blank)		B		81	33.3	58.2
	Armeen S	Formaldehyde	C	25	16	26.3	64.7
	do	do	C	50	9	32.7	69.4
	do	do	C	100	8	37.6	72.3
	(Blank)		C		52	20.5	58.2
13	Armeen C		A	200	11.8	6.8	16.0
	(Blank)		A		107.4	3.0	7.2

EXAMPLE 11

A trimeric formaldimine prepared from formaldehyde and Armeen T was blended in portions of fuel oils B and C at various concentrations. These blends were subjected to the 80° F. and the 110° F. storage tests. Pertinent data therefor are set forth in Table IV.

EXAMPLE 12

A trimeric formaldimine prepared from formaldehyde and Armeen S was blended in portions of fuel oils B and C at various concentrations. These blends were subjected to the 80° F. and the 110° F. storage tests. Pertinent data therefor are set forth in Table IV.

EXAMPLE 13

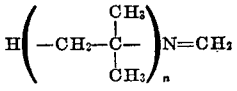
A trimeric formaldimine prepared from formaldehyde and Armeen C was blended in fuel oil A. The blend was subjected to the 80° F. and the 110° F. storage tests. Pertinent data therefor are set forth in Table IV.

It will be apparent from the data in Table IV that the trimeric formaldimines derived from primary aliphatic amines having between about 8 and about 18 carbon atoms effectively improve the color characteristics of fuel oils, as well as inhibit sedimentation. As is to be expected, results vary from oil to oil. However, the overall pattern shows definite improvement of the properties of the fuel oils.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention. Such variations and modifications are considered to be within the scope and purview of the appended claims.

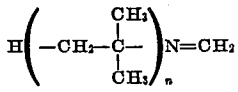
What is claimed is:

1. A distillate fuel oil containing a small amount, sufficient to improve the color stability and the resistance to sedimentation thereof, of an additive selected from the group consisting of (1) a formaldimine having the formula,



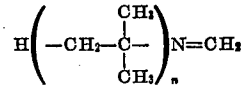
wherein n is an integer of between about one and about six, (2) mixtures of formaldimines of type (1), (3) a formaldimine having the formula $(RN{=}CH_2)_3$, wherein R is a normal aliphatic monovalent hydrocarbon radical containing between about 8 carbon atoms and about 18 carbon atoms per radical, and (4) mixtures of formaldimines of type (3).

2. A distillate fuel oil containing between about 10 pounds per thousand barrels of oil and about 200 pounds per thousand barrels of oil of a formaldimine having the formula,



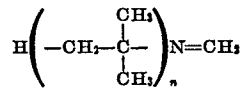
wherein n is 2.

3. A distillate fuel oil containing between about 10 pounds per thousand barrels of oil and about 200 pounds per thousand barrels of oil of a mixture of formaldimines having the formula,



wherein n is an integer of between about one and about six; the average number of carbon atoms in said mixture of formaldimines being between about 18 and about 24.

4. A distillate fuel oil containing between about 10 pounds per thousand barrels of oil and about 200 pounds per thousand barrels of oil of a mixture of formaldimines having the formula,



wherein n is an integer of between about one and about six; the average number of carbon atoms in said mixture of formaldimines being between about 12 and about 15.

5. A distillate fuel oil containing between about 10 pounds per thousand barrels of oil and about 200 pounds per thousand barrels of oil of a mixture of formaldimines having the formula, $(RN{=}CH_2)_3$, wherein R is a normal aliphatic monovalent hydrocarbon radical containing between about 16 carbon atoms and about 18 carbon atoms per radical.

6. A distillate fuel oil containing between about 10 pounds per thousand barrels of oil and about 200 pounds per thousand barrels of oil of a mixture of formaldimines having the formula, $(RN{=}CH_2)_3$, wherein R is a normal aliphatic monovalent hydrocarbon radical containing between about 8 carbon atoms and about 18 carbon atoms per radical.

References Cited in the file of this patent

UNITED STATES PATENTS

1,594,983	Somerville	Aug. 3, 1926
2,560,633	Stedman	July 17, 1951