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STABILIZATION OF PETROLEUM HYDROCARBONS

Charles J. Pedersen, Penns Grove, N. J., and Richard O. Bender, Ridley Park, Pa., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the stabilization of petroleum hydrocarbons and more particularly to the stabilization of distillate fuel oils containing or in contact with copper and its compounds.

It is known that petroleum hydrocarbons, and particularly distillate fuel oils, tend to deteriorate when stored in free contact with the atmosphere. Such deterioration results in the formation and deposition of gelatinous, waxy or gummy materials. These materials foul and clog screens, strainers, small orifices and the like, thereby interfering with the proper functioning of the oil burners, in which the fuels are employed, and rendering the fuel oils unsatisfactory for use. Such deterioration of the fuel oils is accelerated by copper and its catalytically active compounds. Since many oil burner installations include parts made of copper or copper-containing metals, the fuel oils employed therein become exposed to the action of this catalytically active element, whereby their deterioration is rapidly accelerated.

Many compounds, generally termed antioxidants, have been found to inhibit the deterioration of petroleum hydrocarbons caused by oxygen. In general, such antioxidants are relatively ineffective in the presence of catalytically active metals, such as copper and its compounds.

More recently, it has been found that a number of chemical compounds, when incorporated in petroleum hydrocarbons containing catalytically active metals, will react with the catalytically active metals to render such metals catalytically inactive. Such compounds are generally termed metal deactivators. The metal deactivators have little or no antioxidant properties, but merely render the catalytically active metals inactive, so that the petroleum hydrocarbons have substantially the same stability as they would ordinarily have in the absence of the catalytically active metals. Therefore, it is generally desirable to employ an antioxidant with a metal deactivator in petroleum hydrocarbons containing a catalytically active metal. Thereby, the metal deactivator renders the metal catalytically inactive and enables the antioxidant effectively to stabilize the petroleum hydrocarbon as though no catalytically active metal was present.

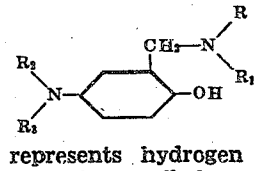
It is an object of the present invention to provide an improved method for the stabilization of petroleum hydrocarbons and particularly of the more volatile and less viscous petroleum hydrocarbons. A more particular object of this invention is to provide an improved method for the stabilization of distillate fuel oils. Another object is to provide petroleum hydrocarbons of improved stability, particularly in the presence of copper and its catalytically active compound. A further object is to provide distillate fuel oils of improved stability. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

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The above and other objects may be accomplished in accordance with our invention which comprises incorporating in the less viscous petroleum hydrocarbons, such as those boiling below 760° F., which are normally subject to deterioration on storage, a small proportion of a 2-aminomethyl-4-aminophenol in which 1 to 2 amino hydrogens of the aminomethyl group are substituted by alkyl groups and 0 to 2 amino hydrogens of the 4-amino group are substituted by alkyl groups. We have found that such compounds are very effective to stabilize petroleum hydrocarbons to produce compositions which will have greatly improved stability toward deterioration on storage. We have also found that such compounds are resistant to the action of catalytically active metal compounds, such as copper and its compounds, whereby they are very effective in stabilizing the petroleum hydrocarbons even in the presence of such catalytically active metals. This latter property is of particular value since, as has been pointed out hereinbefore, most antioxidants are substantially ineffective in the presence of such catalytically active metals. We believe this is due to the fact that our compounds have some metal deactivating properties as well as antioxidant properties.

The petroleum hydrocarbons, which we propose to treat in accordance with our invention, are those which boil below 760° F. and are normally subject to deterioration on storage. Such hydrocarbons will include cracked gasoline and Diesel fuels, but we have found that our invention is of particular value in the treatment of distillate fuel oils and are most beneficial therein. The distillate fuel oils, which are to be treated in accordance with our invention, are the petroleum hydrocarbon fractions which are characterized by a boiling range falling between 250° F. and 760° F. and which are susceptible to oxidative deterioration.

The 2-aminomethyl-4-aminophenol derivatives, which are to be employed in accordance with our invention, may be represented by the formula



wherein R represents hydrogen or an alkyl group, R_1 represents an alkyl group or both R and R_1 together represent an alkylene group in which the terminal carbon atoms are directly bonded to the nitrogen to form with the nitrogen a heterocyclic ring and R_2 and R_3 represent hy-

drogens, alkyl groups or an alkylene group in which the terminal carbon atoms are directly bonded to the nitrogen to form with the nitrogen a heterocyclic ring. Preferably, both R and R_1 represent alkyl radicals and R_2 and R_3 represent hydrogen. Of these compounds, we have found 2-(dimethylaminomethyl)-4-aminophenol to be the most useful for our purpose.

The 2-aminomethyl-4-aminophenol derivatives of our invention may be added to the petroleum hydrocarbons within a wide range of proportions depending upon the degree of stabilization desired and the original stability of the hydrocarbon being treated. The stabilizing compounds of our invention may be employed in the proportion of from about 0.001% to about 1% by weight of the hydrocarbons. For practical purposes, however, they will usually be employed in the proportion of from about 0.005% and about 0.1%. The upper concentrations of some of the less oil soluble compounds will be limited by their solubility in the petroleum hydrocarbons.

The stabilizing compounds of our invention may be added directly to the oil or dissolved in a suitable solvent such as benzene, methanol, isopropanol, acetone and the like. They may be added at any suitable step in the process for the manufacture of the petroleum hydrocarbons or to the hydrocarbons after their manufacture.

In order to illustrate our invention and the preferred modes of carrying the same into effect, representative tests are given hereinafter. These tests were conducted by the accelerated method described by J. R. Sabina, R. O. Bender and E. L. Korb in their article, "A method for evaluating the oxidation stability of distillate fuel oil" in

The fuel oil employed in these tests had the following properties:

Pyrolytic history	Thermally cracked
Treatment	None
Gravity, A. P. I. at 60° F	36.2
S. U. S. viscosity at 100° F., sec	32.0
Aniline point, °F	110.5
Carbon residue, 10% bottoms—percent	0.082
Hot air jet gum, mg./100 cc. at 375° F	10
Sulfur—percent	0.25
A. S. T. M. boiling point, °F.:	
Initial	355
10%	412
50%	435
90%	471
End point	496

The results, obtained with such fuel oil containing 2-(dimethylaminomethyl)-4-aminophenol as the stabilizer, are shown in Table I.

Table I

Test conditions: 15 hours at 212±4° F. and 120 pounds per square inch oxygen pressure. Copper, when present, 1 inch 18 gauge wire per 50 cc. oil.

No.	Conc. stabilizer, wt. per cent	Residues, mg./100 cc.	
		No metal	Copper
1	0	560	2,600
2	0.005	339	799
3	0.01		392-440
4	0.02	351	387

It will be noted that 2-(dimethylaminomethyl)-4-aminophenol retards the formation of residues both in the absence and the presence of copper.

The stabilizer may be used with advantage in combination with other compounds, such as

4-(n-butylamino)-phenol. This is shown in Table II.

Table II

Test conditions: 15 hours at 212±4° F. and 120 pounds per square inch oxygen pressure. Concentration of 4-(n-butylamino)-phenol 0.01% by weight. Copper, when present, 1 inch 18 gauge wire per 50 cc. oil

No.	Conc. 2-(dimethylaminomethyl)-4-aminophenol, weight, per cent	Residues, mg./100 cc.	
		No metal	Copper
1	0	243	1,325
2	0.01	162	251

The beneficial effects of the stabilizer are also revealed by the results of storage tests. Different samples of thermally cracked distillate fuels were stored in the presence of metallic copper.

Table III

Test conditions: Glass containers vented to the atmosphere and stored in the dark at room temperature. Copper 2 sq. cm. surface area per 100 cc. fuel. Residues determined by the hot air jet method.

No.	Fuel No.	Treatment	Days of storage	Residues, mg./100 cc.
1	F-463	None (control)	103	728
	F-463	0.005% 2-(dimethylaminomethyl)-4-aminophenol.	103	167
2	F-509	None (control)	186	497
	F-509	0.01% 2-(dimethylaminomethyl)-4-aminophenol.	186	67
3	F-517	None (control)	189	266
	F-517	0.005% 2-(dimethylaminomethyl)-4-aminophenol.	189	39

It will be apparent that the above tests are given for illustrative purposes only and that our invention is not to be limited to the specific embodiment disclosed therein. It will be readily apparent to those skilled in the art that many variations and modifications can be made particularly in the stabilizing compounds employed, their proportions and in the other ingredients of the compositions. For example, the following compounds are fuel oil stabilizers which are representative of the compounds within our invention:

2-(dimethylaminomethyl) - 4 - dimethylaminophenol
2-(dicyclohexylaminomethyl) - 4 - methylaminophenol
2-(cyclohexylaminomethyl) - 4 - isobutylaminophenol
2-(diethylaminomethyl) - 4 - (n-butylamino)-phenol
2-(dibutylaminomethyl)-4-aminophenol
2 - (diamylaminomethyl)-4-methylaminophenol
2-(amylaminomethyl)-4-amylaminophenol
2-(pentamethyleneaminomethyl) - 4 - isobutylaminophenol
2 - (isopropylaminomethyl) - 4 - isopropylaminophenol
2 - (dodecylaminomethyl) - 4 - dimethylaminophenol
2-(oleylaminomethyl)-4-aminophenol

Our stabilizers may be employed with other antioxidants or with metal deactivators or with both another antioxidant and a metal deactivator. Also, the petroleum hydrocarbons may contain additives, such as ignition promoters, pour point suppressors and the like.

The stabilizing compounds of our invention may be prepared in a known manner by reacting p-nitrophenol with formaldehyde and a pri-

mary or secondary aliphatic amine to produce the 2-aminomethyl-4-nitrophenol followed by reduction of the nitro group and, if desired, by alkylation of the 4-amino group. Still other methods for preparing compounds of this character are disclosed in the literature.

The petroleum hyldrocarbons boiling below 760° F., and particularly the distillate fuel oils and cracked gasoline, are usually unstable. It has been proposed to render such petroleum hydrocarbons more stable by chemical refining methods such as treatment with sulfuric acid. Such refining methods are quite costly and result in large material losses. Our invention is of great advantage in that, by its use, it is possible to stabilize the petroleum hydrocarbons adequately over long periods of time at a reasonable cost without involving any material loss. Our invention is particularly valuable where the petroleum hydrocarbons contain or are in contact with or will be brought into contact with copper and its catalytically active compounds as, by our invention, it is possible to obtain effective stabilization of the hydrocarbons under such conditions by the addition of a single compound.

We claim:

1. Petroleum hydrocarbons, boiling below 760° F. and normally subject to deterioration on storage having incorporated therein, in a small proportion sufficient to inhibit such deterioration, a 2-aminomethyl-4-aminophenol in which 1 to 2 amino hydrogens of the aminomethyl group are substituted by alkyl groups and 0 to 2 amino hydrogens of the 4-amino group are substituted by alkyl groups.

2. A distillate fuel oil, normally subject to deterioration on storage having incorporated therein, in a small proportion sufficient to inhibit such deterioration, a 2-aminomethyl-4-aminophenol in which 1 to 2 amino hydrogens of the aminomethyl group are substituted by alkyl groups and 0 to 2 amino hydrogens of the 4-amino group are substituted by alkyl groups.

3. A distillate fuel oil, normally subject to deterioration on storage having incorporated therein, in a small proportion sufficient to inhibit such deterioration, a 2-aminomethyl-4-aminophenol in which the 2 amino hydrogens of the aminomethyl group are substituted by alkyl groups and 0 to 2 amino hydrogens of the 4-amino group are substituted by alkyl groups.

4. A distillate fuel oil, normally subject to deterioration on storage having incorporated therein, in a small proportion sufficient to inhibit such deterioration, a 2-aminomethyl-4-aminophenol in which 1 to 2 amino hydrogens of the aminomethyl group are substituted by alkyl groups.

5. A distillate fuel oil, normally subject to deterioration on storage having incorporated therein, in a small proportion sufficient to inhibit such deterioration, 2-(dimethylaminomethyl)-4-aminophenol.

CHARLES J. PEDERSEN.
RICHARD O. BENDER.