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UNITED STATES PATENT OFFICE

2,382,906

STABILIZATION OF PETROLEUM HYDROCARBONS

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No Drawing. Application August 21, 1943, Serial No. 499,553

18 Claims. (Cl. 44—63)

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.

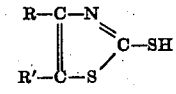
Many compounds, generally termed antioxidants, have been found to inhibit the deterioration of petroleum hydrocarbons caused by oxygen. In general, such antioxidants are relatively ineffective in the presence of catalytically active metals, such as copper and its compounds.

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. The effects of the antioxidant and of the metal deactivator are limited. The antioxidant is itself gradually oxidized and hence used up by contact with fresh quantities of oxygen. The metal deactivator is also frequently used up by being brought into contact with fresh quantities of the catalytically active metal.

It is an object of the present invention to provide an improved method for the stabilization of petroleum hydrocarbons and particularly of distillate fuel oils containing or in contact with copper and its catalytically active compounds. Another object is to provide a method for improving the effectiveness and life of antioxidants and metal deactivators in petroleum hydrocarbons. A further object is to provide petroleum hydrocarbons, and particularly distillate fuel oils of improved stability, especially in the presence of copper and its catalytically active compounds. 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 our invention which comprises incorporating in petroleum hydrocarbons, normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen, a small proportion of an antioxidant, normally effective to substantially inhibit deterioration of the petroleum hydrocarbons in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion of a 2-mercaptothiazole of the formula



wherein each of R and R′ represents a member of the group of hydrogen and hydrocarbon radicals. We have found that the 2-mercaptothiazoles of the above formula render the antioxidants and the copper deactivators more effective to stabilize the petroleum hydrocarbons, whereby the resulting composition is of substantially improved stability. Also, the 2-mercaptothiazoles, employed in accordance with our invention, appear to render the antioxidants and metal deactivators effective over longer periods of time.

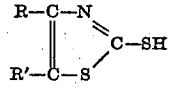
While petroleum hydrocarbons generally may be treated in accordance with our invention, we have found that our invention is of particular utility in the treatment of distillate fuel oils and are most beneficial therein. The distillate fuel oils, which are to be treated in accordance with our invention, are the pertoleum hydrocarbon fractions which are characterized by a boiling range falling between 250° F. and 760° F. and which are susceptible to oxidative deterioration.

Any of the usual antioxidants, known to inhibit oxidative deterioration of the particular type of petroleum hydrocarbon being treated, may be employed. In the treatment of the distillate fuel oils, the antioxidant will generally be an aromatic compound of the class known as gum inhibitors or gasoline antioxidants which include polyhydric phenols, aminophenols and aromatic polyamines, such as 1,2-dihydroxybenzene, 1,5-dihydroxynaphthalene, 4-(n-butylamino)-phenol, 4-isobutylamino-phenol, 1-amino-4-cyclohexylamino benzene and 1,4-(sec-butylamino)-benzene.

The metal deactivators, to be employed in the

combination of our invention, may be any of the metal deactivators which are known to deactivate copper and which, therefore, are more specifically termed copper deactivators. Such copper deactivators include: the condensation products of aromatic ortho-hydroxy-carbonyl compounds with aliphatic primary polyamines disclosed in Patent 2,181,121 to Downing et al.; the di-(2-hydroxy aromatic ketone) ethylenediamines disclosed in Patent 2,255,597 to Downing et al.; the hydroxamic acids disclosed in Patent 2,279,973 to Dietrich; the beta-aminoethyl sulfides and related compounds disclosed in Patent 2,282,710 to Dietrich; the aromatic ortho-hydroxy-carbonyl oximes disclosed in the application of Frederick B. Downing and Charles J. Pedersen Serial No. 303,712 filed November 3, 1939; the condensation products of aliphatic beta-di-ketones with aliphatic primary polyamines, such as 1,2-bis-(methyl-acetonylmethyleneimino)-ethylene; the condensation products of aromatic ortho-hydroxyaldehydes with hydroxyamines, particularly orthoaminophenol, disclosed in the copending application of Frederick B. Downing and Charles J. Pedersen Serial No. 412,602 filed September 27, 1941; the condensation products of ortho-hydroxy aromatic aldehydes with the alkali metal salts of primary amino carboxylic acids as disclosed in the copending application of Frederick B. Downing and Charles J. Pedersen Serial No. 467,554 filed December 1, 1942; the condensation porducts of equimolecular proportions of ortho-hydroxy aromatic aldehydes with primary monoamino polyhydric alcohols as disclosed in the application of Ivan Gubelmann in copending application Serial No. 472,159 filed January 12, 1943; the ortho-hydroxy aryl azo compounds disclosed in the copending application of Charles J. Pedersen Serial No. 461,632 filed October 10, 1942; and the heterocyclic carboxylic acids derived from pyridine and piperidine disclosed in the copending application of Charles J. Pedersen Serial No. 467,555 filed December 1, 1942. Particularly effective copper deactivators are disalicylal propylenediamine, salicylaldoxime, 2-hydroxy-acetophenoxime, 1,2-bis-(methyl-acetonylmethyleneimino)-ethylene and 2-hydroxy-3-methoxybenzal ortho-aminophenol.

The third component, which is to be added to the petroleum hydrocarbons in accordance with our invention, is a 2-mercaptothiazole having the formula



wherein each of R and R' represents hydrogen or a hydrocarbon radical. Preferably, only one of R and R' represents a hydrocarbon radical. The hydrocarbon radicals may be aliphatic, cycloaliphatic, aryl substituted aliphatic, aromatic and alkyl substituted aromatic. Preferably, the hydrocarbon radicals represented by R and R' are aliphatic and particularly short chain aliphatic of 1 to 4 carbon atoms. The following 2-mercaptothiazoles will be found to give satisfactory results in accordance with our invention:

2-mercaptothiazole
2-mercapto-4-methylthiazole
2-mercapto-5-methylthiazole
2-mercapto-4-propylthiazole
2-mercapto-4-ethylthiazole
2-mercapto-4-phenylthiazole
2-mercapto-4,5-dimethylthiazole

The antioxidant, the copper deactivator and the 2-mercaptothiazole may be added to the hydrocarbon within a wide range of proportions depending upon the results desired. They will each be added to the hydrocarbons in a quite small proportion. Usually, the antoxidant will be added in the proportion of from about 0.001% to about 1%. The metal deactivator will ordinarily be employed in the proportion of from about 0.0001% to about 0.1%. The 2-mercaptothiazole will generally be added in the proportion of from about 0.0001% to about 0.01%. These percentage proportions are based on the oil. Also, the concentrations of some of the antioxidants, some of the copper deactivators and some of the 2-mercaptothiazoles will be limited by their solubility in the oil being treated.

The antioxidant, the copper deactivator and the 2-mercaptothiazoles may each be added directly to the oil or dissolved in a solvent, such as benzene, methanol, acetone and the like. They may each be added to the oil separately or mixed together in suitable proportions prior to their addition to the oil. They may be added to the oil in its final stage of manufacture or at any suitable stage in the process of manufacturing the oils.

The effectiveness of this method of treatment is shown by the storage stability data given in the table. Eight hundred cc. of fuel oil in 1 quart vented glass bottles were stored in the dark at atmospheric temperature. The area of contact of the metals when present was 2 sq. cm. per 100 cc. of oil. The residue content, after 227 days of storage, was determined by the hot air jet gum method at 375° F.

The fuel oil used possessed the following properties:

Pyrolytic history	Thermally cracked
Treatment	None
Gravity, A. P. I. at 60° F.	34.5
Aniline point, °F.	96
Carbon residue, 10% bottoms, percent	0.17
Sulfur, do	0.058
A. S. T. M. boiling point, °F.:	
Initial	356
10%	376
50%	428
90%	478
End point	502

Table

No.	Additive	Conc.	Residues after 227 days, mg /100 cc.		
			No metal	Iron	Copper
		Wt. %			
1	None (control)		363	392	560
2	Disalicylal propylenediamine.	0.002	267	225	255
3	Disalicylal propylenediamine.	0.002	79	85	88
	4-(n-butylamino)-phenol.	0.01			
4	Disalicylal propylenediamine.	0.002	60	53	62
	4-(n-butylamino)-phenol.	0.01			
5	2-mercapto-4-methylthiazole.	0.0002			

It will be observed that the disalicylal propylene-diamine (a copper deactivator) retards the formation of residues to some extent. The combination of the disalicylal propylenediamine and 4-(n-butylamino)-phenol (a commercial antioxidant) yields improved results. However, the combination of as little as 0.0002% of 2-mer-

capto-4-methyl-thiazole with the copper deactivator and the antioxidant produced substantially better results. The results, obtained by the combination of the three components, are synergistic rather than additive.

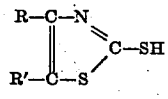
It will be understood that the foregoing tests have been given for illustrative purposes solely and that many variations and modifications may be made therein, particularly in the particular antioxidant, copper deactivator and 2-mercaptothiazole employed, without departing from the spirit or scope of our invention. The antioxidant may be any other antioxidant for the hydrocarbon being treated or may be a mixture of two or more antioxidants. Also, the copper deactivator of the combination may be a mixture of copper deactivators or of any one or more copper deactivators with other metal deactivators. Furthermore, the 2-mercaptothiazole may be a mixture of two or more 2-mercaptothiazoles of the character hereinbefore disclosed. Still further, other addition agents may be employed in the stabilized petroleum hydrocarbons, such as oiliness agents, combustion promoters, pour point depressors, viscosity index improving agents and the like.

Each of 2-mercaptothiazole, 2-mercapto-4-methylthiazole, 2-mercapto-5-methylthiazole, 2-mercapto-4-propylthiazole, 2-mercapto-4-ethylthiazole, 2-mercapto-4-phenylthiazole and 2-mercapto-4,5-dimethylthiazole will be found to be effective in combination with disalicylal propylenediamine and 4-(n-butylamino)-phenol. Other effective combinations may be combinations of catechol, disalicylal propylenediamine and each of the 2-mercaptothiazoles specifically listed above. Still other desirable combinations are combinations of disalicylal propylenediamine, 1,4-di-(sec-butylamino)-benzene and 2-mercapto-4-methylthiazole or any of the other 2-mercaptothiazoles specifically listed above.

It has been usual to improve the stability of fuel oils by subjecting them to some chemical refining method, such as treatment with sulfuric acid. Such methods, however, are relatively costly and result in material losses. By employing the combination of an antioxidant, a copper deactivator and a 2-mercaptothiazole in accordance with our invention, we have found it possible to stabilize distillate fuel oil adequately at a very reasonable cost and without any material loss. Accordingly, our invention results in substantial economies and other results which are of value to the art.

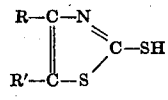
We claim:

1. Petroleum hydrocarbons normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the petroleum hydrocarbons in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



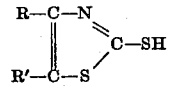
wherein R and R' represent members of the group consisting of hydrogen and hydrocarbon radicals.

2. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



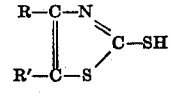
wherein R and R' represent members of the group consisting of hydrogen and hydrocarbon radicals.

3. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



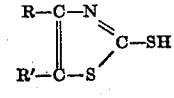
wherein one of R and R' represents a hydrocarbon radical and the other represents a member of the group consisting of hydrogen and hydrocarbon radicals.

4. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



wherein one of R and R' represents a hydrocarbon radical and the other represents hydrogen.

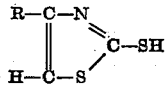
5. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercapto thiazole of the formula



wherein R and R' represent aliphatic hydrocarbon radicals.

6. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small pro-

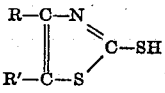
portion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



wherein R represents an aliphatic hydrocarbon radical.

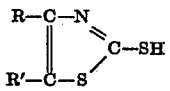
7. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of 2-mercapto-4-methylthiazole.

8. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of 4-(n-butylamino)-phenol, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



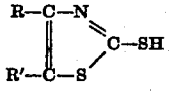
wherein R and R' represent members of the group consisting of hydrogen and hydrocarbon radicals.

9. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of disalicylal propylenediamine, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



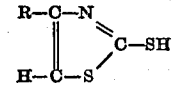
wherein R and R' represent members of the group consisting of hydrogen and hydrocarbon radicals.

10. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of 4-(n-butylamino)-phenol, a small proportion of disalicylal propylenediamine, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



wherein R and R' represent members of the group consisting of hydrogen and hydrocarbon radicals.

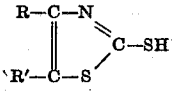
11. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of 4-(n-butylamino)-phenol, a small proportion of disalicylal propylenediamine, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



wherein R represents a short chain aliphatic hydrocarbon radical.

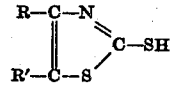
12. A distillate fuel oil normally subject to catalytic deterioration caused by copper and its compounds in the presence of oxygen having incorporated therein a small proportion of 4-(n-butylamino)-phenol, a small proportion of disalicylal propylenediamine, and a small proportion, from about 0.0001% to about 0.01%, of 2-mercapto-4-methylthiazole.

13. The method of inhibiting the catalytic deterioration of petroleum hydrocarbons normally caused by copper and its compounds in the presence of oxygen which comprises incorporating in the petroleum hydrocarbons a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the petroleum hydrocarbons in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



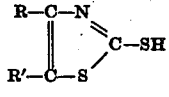
wherein R and R' represent members of the group consisting of hydrogen and hydrocarbon radicals.

14. The method of inhibiting the catalytic deterioration of a distillate fuel oil normally caused by copper and its compounds in the presence of oxygen which comprises incorporating in the fuel oil a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



wherein one of R and R' represents a hydrocarbon radical and the other represents a member of the group consisting of hydrogen and hydrocarbon radicals.

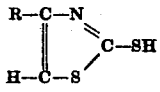
15. The method of inhibiting the catalytic deterioration of a distillate fuel oil normally caused by copper and its compounds in the presence of oxygen which comprises incorporating in the fuel oil a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



wherein one of R and R' represents an aliphatic hydrocarbon radical and the others represents hydrogen.

16. The method of inhibiting the catalytic deterioration of a distillate fuel oil normally caused by copper and its compounds in the presence of

oxygen which comprises incorporating in the fuel oil a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of a 2-mercaptothiazole of the formula



wherein R represents an aliphatic hydrocarbon radical.

17. The method of inhibiting the catalytic deterioration of a distillate fuel oil normally caused by copper and its compounds in the presence of oxygen which comprises incorporating in the fuel oil a small proportion of an antioxidant normally effective to substantially inhibit deterioration of the fuel oil in the absence of copper and its compounds, a small proportion of a copper deactivator, and a small proportion, from about 0.0001% to about 0.01%, of 2-mercapto-4-methylthiazole.

18. The method of inhibiting the catalytic deterioration of a distillate fuel oil normally caused by copper and its compounds in the presence of oxygen which comprises incorporating in the fuel oil a small proportion of 4-(n-butylamino)-phenol, a small proportion of disalicylal propylenediamine, and a small proportion, from about 0.0001% to about 0.01%, of 2-mercapto-4-methylthiazole.

CHARLES J. PEDERSEN.
RICHARD O. BENDER.

Certificate of Correction

Patent No. 2,382,906. August 14, 1945.

CHARLES J. PEDERSEN ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, lines 63 to 67 inclusive, in the table, strike out

4	Disalicylal propylenediamine. 4-(n-butylamino)-phenol
5	2-mercapto-4-methylthiazole.

and insert instead

4	Disalicylal propylenediamine. 4-(n-butylamino)-phenol 2-mercapto-4-methylthiazole.

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of October, A D. 1945.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.