United States Patent Office 2,763,616 Patented Sept. 18, 1956

2,763,616

ALKYLTHIOHYDROQUINONES - FORMALDEHYDE-AMINE REACTION PRODUCTS AND PETROLEUM FRACTIONS CONTAINING THE SAME

John W. Brooks, Wenonah, N. J., assignor to Socony Mobil Oil Company, Inc., a corporation of New York

No Drawing. Application May 24, 1952, Serial No. 289,888

18 Claims. (Cl. 252—47.5)

This invention relates to the stabilization of petroleum fractions, such as lubricating oils and gasolines, against oxidation. More particularly, it relates to addition agents for petroleum fractions which are capable of greatly inhibiting the oxidative deterioration of such fractions.

It is well known that petroleum oil fractions refined for use as lubricants are subject to oxidative deterioration under conditions of use in modern combustion engines. The oxidation products which are formed in the oil are acidic in nature and exert a corrosive effect on the metal parts with which the oil comes in contact. Alloy bearings, such as copper-lead, silver-cadmium, nickel-cadmium, etc., which are widely used, are particularly subject to attack by the acidic oxidation products formed in the oil in use. Furthermore, these oxidation products produce formations of varnish and sludge on the engine surfaces which lower the operating efficiency of the engine. Also, due to oxidation effects, the viscosity of the oil is changed in use so that proper lubrication of the engine parts is not obtained. In the case of turbine oils, the problem of oxidation is increased since the oil normally becomes contaminated with water. Lighter oil fractions, such as kerosene and gasoline, are also subject to oxidative deterioration in storage with the formation of undesirable gum, color bodies, etc. therein. It is an object of this invention to provide a class of addition agents for petroleum oil fractions which are capable of substantially inhibiting the oxidative deterioration of such fractions. A further object is to provide petroleum compositions, such as lubricating oils and gasolines, which are highly stabilized against oxidation under the conditions of use, with respect to the lubricating oils, and in storage with respect to the gasolines.

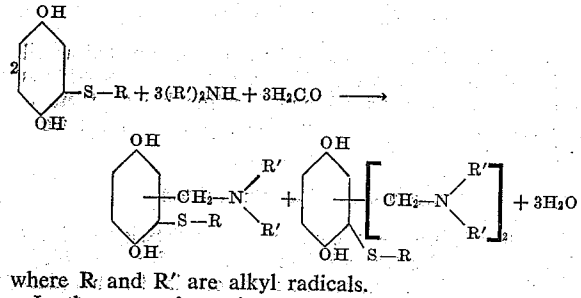
In a copending application, Serial No. 277,300, I have disclosed and claimed oil compositions containing alkylthiohydroquinones as anti-oxidants. Also, I have described and claimed a method for preparing the alkylthioquinones and I have claimed certain tertiary alkylthiohydroquinones as new compositions of matter. I have now found that alkylthiohydroquinones, such as disclosed in that application, can be reacted with formaldehyde and a primary or secondary aliphatic amine to form products which are outstanding anti-oxidants for petroleum oil fractions. As far as is known, these alkylthiohydroquinone-formaldehyde-amine products have not been prepared heretofore and they are, therefore, contemplated herein as new compositions of matter.

The alkylthiohydroquinones contemplated herein for reaction with the formaldehyde and the primary or secondary amine are those having from 1 to about 20 carbon atoms in the thioalkyl substituent groups, for example, monoalkylthio-substituted hydroquinones, such as methylthiohydroquinone, t-butylthiohydroquinone, octylthiohydroquinone, t-dodecylthiohydroquinone and t-octadecylthiohydroquinone and dialkylthio-substituted hydroquinones, such as di-t-butylthiohydroquinone, di-octylthiohydroquinone, didodecylthiohydroquinone and di-octadecylthiohydroquinone.

A method for preparing the alkylthiohydroquinones utilized herein is set forth in the copending application, Serial No. 277,300. As disclosed in said application, the alkythiohydroquinones can be prepared in good yield by the reaction of an aliphatic mercaptan with quinone in the presence of an acidic catalyst, such as p-toluene sulfonic acid, at relatively low temperatures, viz., from about 0° C. to about 100° C.; the best yields being obtained when an excess of mercaptan is used in the reaction, i. e., at least 2 moles of mercaptan per mole of quinone. As further pointed out in the copending application, the higher temperatures within the aforesaid range favor the formation of mono-substituted alkylthiohydroquinones, while the lower temperatures, i. e., from about 0° C. to about 10–15° C., favor the formation of polyalkylthio-substituted hydroquinones.

The amines suitable for reaction with the alkylthiohydroquinones and formaldehyde to form the products herein contemplated are aliphatic, primary amines containing from 1 to about 20 carbon atoms in the alkyl groups thereof. Thus, primary amines, such as ethyl amine, butyl amine, ethylhexyl amine, octyl amine, decyl amine, dodecyl amine, tetradecyl amine, hexadecyl amine and octadecyl amine, and secondary amines, such as di-n-butyl amine, di-2-ethylhexyl amine, di-n-octyl amine, di-n-dodecyl amine, may be used. Also, mixed dialkyl amines in which the different alkyl radicals contain from 1 to about 20 carbon atoms are suitable for the invention.

The reaction of the alkylthiohydroquinone with the formaldehyde and the primary or secondary amine takes place readily at room temperature, i. e., around 15–30° C. The reactants are preferably utilized in the ratio of at least 2 moles of formaldehyde and 2 moles of the amine per mole of the alkylthiohydroquinone. The reaction is generally completed in from about ½ hour to about 3 hours. The reaction mechanism is that of the Mannich reaction ("Organic Reactions," Adams et al., vol. I, chap. 10, John Wiley and Sons, 1942). Where the amine involved is a secondary amine, the reaction is clear cut, the product analyses indicating the formation of a mixture of (1) the alkylthiohydroquinone, mono-substituted with the dialkylaminomethyl group ($—CH_2—N(R)_2$) and (2) the alkylthioquinone, di-substituted with the dialkylaminomethyl group. The reaction can be represented as follows:



where R and R′ are alkyl radicals.

In the case of a primary amine, however, the products of the reaction are not precisely known, since the initial condensation provides alkylthiohydroquinone, substituted with methylalkylamine groups which still have a hydrogen available for further condensation with unreacted alkylthiohydroquinone. The product is, therefore, a complex mixture which defies exact analysis but which is most likely composed of (1) alkylthiohydroquinone, mono-substituted with the mono-alkylaminomethyl ($—CH_2—N(H)R$) radical, (2) the alkylthiohydroquinone, di-substituted with the mono-alkylaminomethyl radical, and additional products formed by further reaction of products 1 and 2 with unreacted alkylthiohydroquinone.

Table I summarizes the results obtained by reacting alkylthiohydroquinones with formaldehyde and representative primary and secondary amines. All of these reactions were conducted under approximately the following conditions. A ratio of 1 mole of the alkylthiohydroquinone to 3 moles of the amine and 3 moles of formaldehyde (in the form of a 36 per cent aqueous mixture) was used. The alkylthiohydroquinone was first mixed with the amine and the formaldehyde solution was added with stirring over a period of about ½ hour with the temperature of the reaction mixture being maintained at about 20–25° C. The reaction mixture was then stirred for several hours at room temperature, the water separated out, and then topped to a pot temperature of 150–175° C. under 2 mm. pressure to obtain the final product. It will be seen from the data in Table I that the product from Example 2 is mainly the di-dialkylaminomethyl-substituted alkylthiohydroquinone, the products of Examples 3 and 4 are mixtures of the alkylthiohydroquinone (*a*) mono-substituted with the dialkylaminomethyl group and (*b*) di-substituted with the dialkylaminomethyl group, and the product from Example 5 is mainly the mono-dialkylaminomethyl-substituted alkylthiohydroquinone.

of turbine oils. In this test, a 100-gram sample of test oil is used. An aluminum constant temperature block is used as a heating bath. The bath is maintained at a temperature of 203° F. The test tubes are 250 mm. x 25 mm. in size and are provided with a finger tube condenser and an oxygen delivery tube. A catalyst coil prepared by interwinding 20 inches of No. 18 copper wire with 20 inches of No. 18 iron wire is placed in each tube. Four tubes, each containing 25 ml. of oil, are used for each test oil. Five ml. of distilled water is introduced into each tube and 0.3±0.05 liter of oxygen per hour are passed through each tube for the duration of the test. Water is added when necessary to keep a volume of 5 ml. present. The tubes are removed one tube at a time at desired intervals and the Lovibond color and N. N. (neutralization number) of the oil determined.

The reference oil used in both the Brown-Boveri and A. S. T. M. oxidation test was a solvent-refined, Mid-Continent distillate having a specific gravity of 0.86, a flash point of 405° F. and a viscosity of 155 S. U. S. at 100° F. The results obtained are shown in Table II.

TABLE I

Reaction of amines with alkylthiohydroquinones

Example Number	Reactants	Product	Yield, Wt. (G.)	Analyses, Wt. Percent N	Analyses, Wt. Percent S
1	10 g. (0.05 mol) t-butylthiohydroquinone 27 g. (0.15 mol) 25% aqueous dimethylamine 13 g. (0.15 mol) 36% aqueous formaldehyde		11		
2	15 g. (0.075 mol) t-butylthiohydroquinone 29 g. (0.225 mol) di-n-butylamine 19.5 g. (0.225 mol) 36% aqueous formaldehyde	Mainly tert.-butylthio-bis-(di-n-butylaminomethyl)-hydroquinone.	37	6.56 [1] 5.83	6.25 [1] 6.67
3	15 g. (0.075 mol) t-butylthiohydroquinone 36 g. (0.15 mol) di-2-ethylhexylamine 13 g. (0.15 mol) 36% aqueous formaldehyde	Mixture of (1) tert.-butylthio-di-2-ethylhexylaminomethylhydroquinone and (2) tert.-butylthio-bis-(di-2-ethylhexyl-aminomethyl)-hydroquinone.	21	3.66 [2] 3.11 [1] 3.98	6.38 [2] 7.12 [1] 4.54
4	51 g. (0.2 mol) t-octylthiohydroquinone 78 g. (0.6 mol) di-n-butylamine 50 g. (0.6 mol) 36% aqueous formaldehyde	Mixture of (1) tert.-octylthio-di-n-butylaminomethylhydroquinone and (2) tert.-octylthio-bis (di-n-butylaminomethyl)-hydroquinone.	94	4.34 [2] 3.56 [1] 5.23	7.17 [2] 8.15 [1] 5.98
5	32 g. (0.1 mol) t-dodecylthiohydroquinone 39 g. (0.3 mol) di-n-butylamine 25 g. (0.3 mol) 36% aqeous formaldehyde	Mainly tert.-dodecylthio-di-n-butylaminomethylhydroquinone.	50	3.04 [2] 3.12	7.84 [2] 7.14
6	26 g. (0.08 mol) t-dodecylthiohydroquinone 15 g. (0.2 mol) n-butylamine 17 g. (0.2 mol) 36% aqueous formaldehyde		29	2.26	10.65

[1] Calculated values for disubstituted product.
[2] Calculated values for mono-substituted product.

Anti-oxidant action

The ability of the products herein contemplated as oil anti-oxidants has been demonstrated by a number of tests conducted on various oil and gasoline blends thereof. The test procedures used and the results obtained were as follows:

Brown-Boveri turbine oil test

This test determines the oxidation characteristics of turbine oils. In this test a 200-ml. sample of the test oil is placed in a 400-ml. tall form beaker provided with a glass cover having a center hole for the entrance of air. A polished copper plate (70 mm. x 40 mm. x 1 mm.) is bent into a V shape and placed in the beaker so that the 70 mm. edge forms the base. The beaker is placed in a constant temperature oil bath maintained at 230° F. Air is passed over the surface of the test oil at a rate of 2 liters per hour for 72 hours. The beaker is then removed from the bath and allowed to stand for 24 hours at room temperature. The Lovibond color and the N. N. (neutralization number) of the oil are then determined.

The A. S. T. M. oxidation test

This test also determines the oxidation characteristics

TABLE II

Brown-Boveri and A. S. T. M. oxidation tests

Product added	B.-B.[1] Oxidation Test: Wt. percent Concn.	B.-B.[1] Oxidation Test: Lovibond Color	B.-B.[1] Oxidation Test: N. N.	A. S. T. M. Oxidation Test: Wt. percent Concn.	A. S. T. M. Oxidation Test: Hrs.	A. S. T. M. Oxidation Test: Lovibond Color	A. S. T. M. Oxidation Test: N. N.
None	-------	55	0.24	-------	0	0.1	0.01
					24	3	0.05
					72	172	5.1
Example No. 2	0.2	10	0.01	-------	-------	-------	-------
Example No. 3	0.2	6	0.05	0.2	0	10	0
					408	21	0.02

[1] Brown-Boveri.

The bubble test

This test determines the relative tendency of lubricating oils to corrode metal bearings. In this test, a connecting rod bearing having a cadmium-silver alloy surface is carefully weighed (about 6 grams) and is placed in a 20 mm. x 25 mm. test tube together with 30 grams of the test oil. A 5 mm. glass inlet tube, drawn to about 1 mm. I. D. for about 30 mm. at one end is placed in the tube. The test tube is placed in a constant temperature bath maintained at 175° C. and air is blown through the test oil at a rate

of 2 liters per hour for 22 hours. The test piece is then removed and weighed. The results are represented in milligrams of weight loss. The reference oil used in all of these tests consisted of neutral and residuum stocks separately refined by means of chlorex and then blended to give an S. A. E. motor oil having a specific gravity of 0.872, a flash point of 435° F., and a Saybolt Universal viscosity of 318 seconds at 100° F. The results of these tests are shown in Table III.

TABLE III

Bubble test

Product Added	Wt. Percent Concn.	Mg. Less in Wt.
None		20
Example No. 2	0.25	0
Example No. 3	0.25	0
Example No. 4	0.25	0
Example No. 5	0.25	0
Example No. 6	<0.5	0

The German tar test

This test determines the antioxidant properties of an oil. In this test, a 150-gram oil sample is placed in a 250 ml. extraction flask in an oil bath maintained at 120° C. The flask is equipped with a cork having a 6 mm. I. D. inlet tube extending therethrough to the bottom of the flask and a vent tube. Oxygen gas is bubbled through the oil at the rate of 2 bubbles per second for 70 hours. The N. N. (neutralization number) of the oil is then measured. The reference oil used for this test was a highly acid-refined coastal distillate suitable for use in transformers. It had a specific gravity of 0.871, a flash point of 310° F., and a Saybolt Universal viscosity of 69 seconds at 100° F. The results of these tests are summarized in Table IV.

TABLE IV

German tar test

Product Added	Wt. Percent Concn.	N. N.
None		18
Example No. 2	0.1	0.05
Example No. 3	0.1	0.05
Example No. 4	0.1	0.02
Example No. 5	0.1	0.02
Example No. 6	0.1	0.03

The Lauson oxidation stability test

This test determines oil deterioration as measured by corrosion of copper-lead bearings. In this test, one gallon of oil is used in a Lauson single-cylinder, 4-cycle, liquid-cooled gasoline engine with splash lubrication, the engine having a weighed copper-lead bearing. The engine is operated under the following conditions for 100 hours.

Oil temperature—270° F.
Jacket temperature—212° F.
Speed—1825 R. P. M.
One-half throttle
13–1 air-fuel ratio
Oil added every 20 hours

The fuel used was a controlled "Mobilgas Special" blend (40% thermal, 30% catalytically cracked and 30% straight run plus 2.5 cc. tetraethyl lead per gal.). The engine bearing is weighed at the end of the test to determine the weight loss thereof. The results are shown in Table V. The reference oil used was the same as that used in the Bubble Test.

TABLE V

Lauson OS–2 oxidation test

Product Added	Wt. Percent Concn.	Bearing Wt. Loss (G) Av. of Top and Bottom
None		0.510
Example No. 4	0.5	0.080

Gasoline storage test

This test determines the gram stability of gasoline under simulated field storage conditions. In this test, 2 or more 1500-ml. samples of the gasoline are stored in half-gallon brown bottles with 200 ml. of distilled water and $2\frac{11}{16}$ in. by 9 in. polished iron strips in each bottle. The bottles are filled with a slotted cork to permit breathing of the samples and at the same time prevent contamination by foreign matter. The samples are stored in a room at a temperature of 70 to 80° F. The samples are tested in turn at specified time intervals and then discarded. The glass dish gum formed during the period of storage up to the time of the test is taken as a measure of the gum stability of the gasoline. The reference gasoline used in these tests was a KOH-treated thermal gasoline. The results are shown in Table VI.

TABLE VI

Gasoline storage test

Gasoline Tested	Glass Dish Gum, Mg. Gum/100 Ml.	
	20 Days	50 Days
KOH-treated thermal gasoline	97.3	279
KOH-treated thermal gasoline containing 10 lb./1,000 bbls. of Example No. 2	4.9	6.6

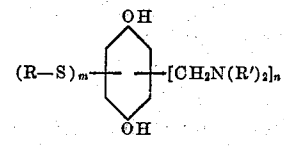
From the test results given in the foregoing tables, it can be seen that the reaction products contemplated herein are highly effective for stabilizing petroleum fractions against the deteriorating effects of oxidation.

The amount of the alkylhydroquinone-formaldehyde-amine product to be added to a petroleum oil fraction will vary somewhat with the particular oil fraction and the conditions of use. Amounts ranging from about 0.01 per cent, by weight, to about 10 per cent, by weight, may be used, although usually from about 0.1 per cent to about 2 per cent provide satisfactory oxidation inhibition. The additives of this invention may, of course, be added to petroleum fractions along with other additive agents designed to improve various other characteristics of such fractions, e. g., pour depressants, extreme pressure agents, detergents and the like.

Although the invention has been illustrated herein by the use of specific examples of my additive products and in particular petroleum media, it is not intended that the scope of my invention be in any way limited thereby, but only as shown in the accompanying claims.

What is claimed is:

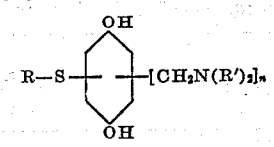
1. A petroleum lubricating oil containing a minor amount, sufficient to stabilize said oil against oxidation, of a compound of the formula



where R and R' are alkyl radicals having from 1 to about 20 carbon atoms, and *m* and *n* are integers from 1 to 2.

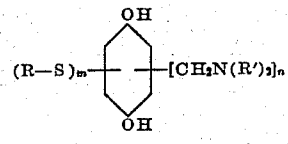
2. A petroleum lubricating oil containing a minor

amount, sufficient to stabilize said oil against oxidation, of a compound of the formula



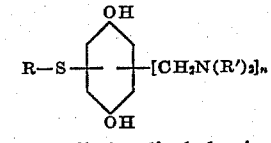
where R and R' are alkyl radicals having from 1 to about 20 carbon atoms, and *n* is an integer from 1 to 2.

3. A gasoline containing a minor amount, sufficient to stabilize said gasoline against oxidation, of a compound of the formula



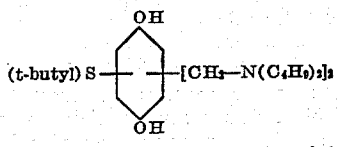
where R and R' are alkyl radicals having from 1 to about 20 carbon atoms, and *m* and *n* are integers from 1 to 2.

4. A gasoline containing a minor amount, sufficient to stabilize said gasoline against oxidation, of a compound of the formula

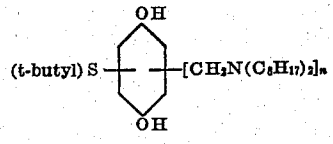


where R and R' are alkyl radicals having from 1 to about 20 carbon atoms, and *n* is an integer from 1 to 2.

5. A petroleum lubricating oil containing a minor amount, sufficient to stabilize said oil against oxidation, of a compound of the formula

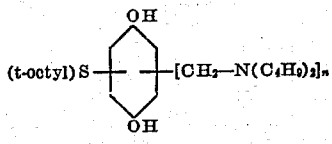


6. A petroleum lubricating oil containing a minor amount, sufficient to stabilize said oil against oxidation, of a compound of the formula



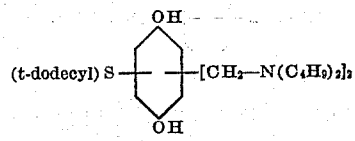
where *n* is an integer from 1 to 2.

7. A petroleum lubricating oil containing a minor amount, sufficient to stabilize said oil against oxidation, of a compound of the formula

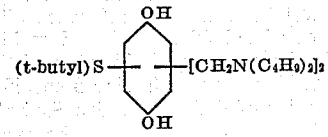


where *n* is an integer from 1 to 2.

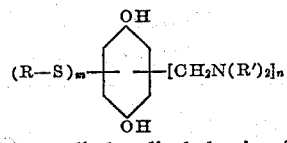
8. A petroleum lubricating oil containing a minor amount, sufficient to stabilize said oil against oxidation, of a compound of the formula



9. A gasoline containing a minor amount, sufficient to stabilize said gasoline against oxidation, of a compound of the formula

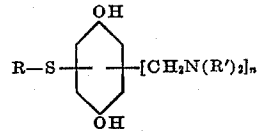


10. As a new composition of matter, a compound of the formula



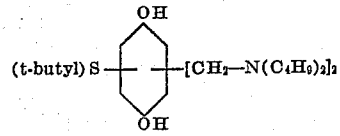
where R and R' are alkyl radicals having from 1 to about 20 carbon atoms, and *m* and *n* are integers from 1 to 2.

11. As a new composition of matter, a compound of the formula

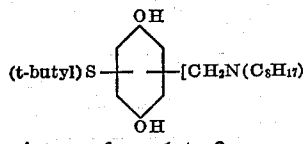


where R and R' are alkyl radicals having from 1 to about 20 carbon atoms, and *n* is an integer from 1 to 2.

12. As a new composition of matter, a compound of the formula

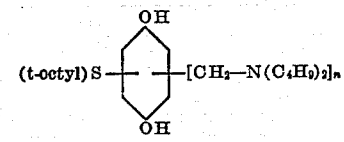


13. As a new composition of matter, a compound of the formula



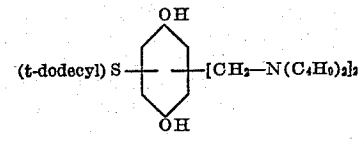
where *n* is an integer from 1 to 2.

14. As a new composition of matter, a compound of the formula



where *n* is an integer from 1 to 2.

15. As a new composition of matter, a compound of the formula



16. A petroleum fraction containing a minor amount, sufficient to stabilize said fraction against oxidation, of a sulfur- and nitrogen-containing reaction product formed by reacting (1) an alkylthio-substituted hydroquinone having no substituents other than unsubstituted alkylthio groups, said alkylthio groups containing from 1 to about 20 carbon atoms and being attached through the sulfur atom thereof to the hydroquinone nucleus, with (2) formaldehyde and (3) a primary aliphatic amine having from 1 to about 20 carbon atoms per alkyl group thereof, at a temperature of from about 15° C to about 30° C., and for a time period of from about ½ hour to several hours.

17. As a new composition of matter, a sulfur- and

nitrogen-containing reaction product formed by reacting (1) an alkylthio-substituted hydroquinone having no substituents other than unsubstituted alkylthio groups, said alkylthio groups containing from 1 to about 20 carbon atoms and being attached through the sulfur atom thereof to the hydroquinone nucleus, with (2) formaldehyde and (3) a primary aliphatic amine having from 1 to about 20 carbon atoms per alkyl group thereof, at a temperature of from about 15° C. to about 30° C., and for a time period of from about ½ hour to several hours.

18. As a new composition of matter, a sulfur- and nitrogen-containing reaction product formed by reacting (1) tertiary dodecylthiohydroquinone with (2) formaldehyde and (3) normal butylamine, at a temperature of from about 15° C. to about 30° C., and for a time period of from about ½ hour to several hours.

References Cited in the file of this patent

UNITED STATES PATENTS

2,553,441 Chenicek ---------- May 15, 1951