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MINERAL OIL COMPOSITION CONTAINING
OXIDATION INHIBITORRobert Cocroft and Elmer W. Brennan, Chicago,
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corporation of OhioNo Drawing. Application July 7, 1945,
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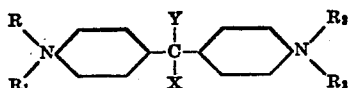
13 Claims. (Cl. 252-51.5)

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This invention relates to oxidation inhibitors and to compositions containing the same.

It is well-known to add small amounts of various additives to hydrocarbon lubricating oils in order to lessen the corrosive effect of such oils on automotive engine bearings and to inhibit oxidation of such oils with the formation of sludge and varnish. Among compounds which have been suggested for this purpose are p,p'-bis-(dimethylamino)-diphenylmethane and p,p'-bis-(dimethylamino)-triphenylmethane.

We have discovered that the effectiveness of compounds of the type above referred to in inhibiting oxidation of oxidizable lubricating liquids can be further improved particularly with respect to inhibiting varnish formation by incorporating in the compound a phenyl ring containing a hydroxy group, an alkoxy group or a combination of the two.

In accordance with our invention there is added to conventional hydrocarbon lubricating oils or other oxidizable compositions which it is desired to inhibit against oxidation approximately .01% or less to 5% by weight and preferably 0.25 to 1% by weight of a compound having the following formula:

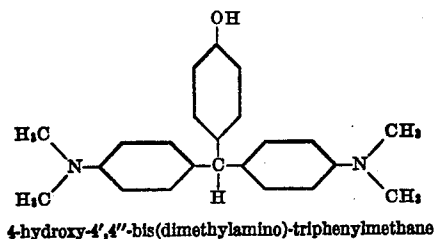
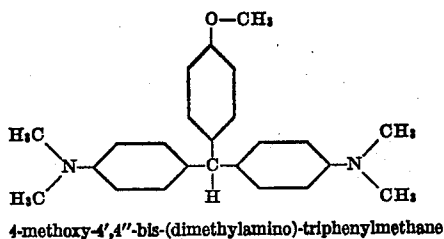
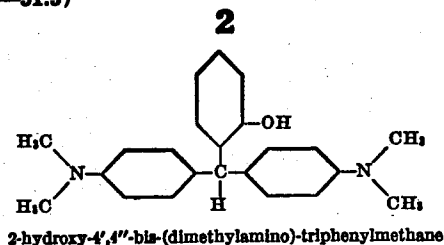
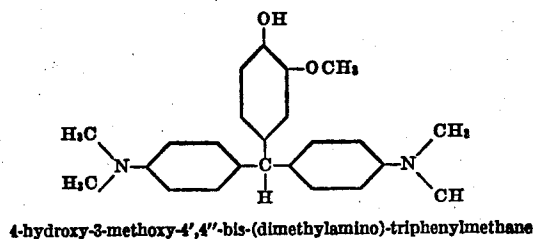
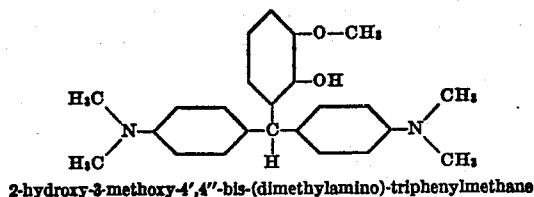
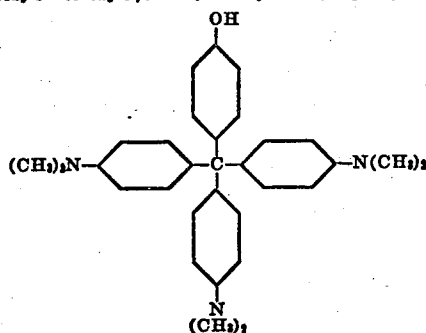
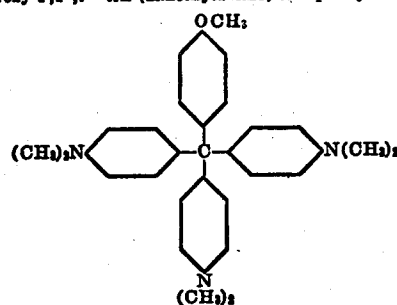


R, R₁, R₂, and R₃ are either hydrogen or alkyl groups.

Y is a phenyl ring containing an hydroxyl or alkoxy group or both.

X is hydrogen, an alkyl, aryl or aralkyl group with or without amino or alkyl substituted amino groups attached thereto.

As examples of specific compounds falling within the scope of our invention are mentioned:



Compounds in accordance with our invention may be added to the mineral lubricating oil in amounts hereinbefore specified and thoroughly mixed with the oil; or the compounds in the form of concentrates, as for example, dissolved in a

portion of the lubricating oil, may be blended with the mineral oil in the engine.

In order to demonstrate the effectiveness of compounds falling within the scope of our invention in inhibiting oxidation of mineral lubricating oils and inhibiting bearing corrosion of automotive engines, a series of Underwood tests were made in which 0.5% by weight of the additive in a Mid-Continent SAE 30 lubricating oil was used. The Underwood tests were run at 325° C. and at a pressure of ten pounds per square inch. The oil was examined after five hours and after ten hours running. The Underwood test is described in an article "Automotive bearing materials and their application," by A. F. Underwood, Journal of Society of Automotive Engineers, volume 43, pages 385 to 392, September, 1938. The results obtained in the tests are tabulated in the following table:

Table I

Additive No.	Additive	Percent Increase in Viscosity at 130° F.		Neutralization No.		Bearing Loss in Grams			
		5 Hr.	10 Hr.	5 Hr.	10 Hr.	CuPb		AgCd	
						5 Hr.	10 Hr.	5 Hr.	10 Hr.
1.....	4-hydroxy-4',4''-bis(dimethylamino)-triphenylmethane.....	9.1	13.1	-----	0.35	0.0010	0.0015	0.0180	0.0100
2.....	4-methoxy-4',4''-bis(dimethylamino)-triphenylmethane.....	14.7	25.0	0.75	1.13	0.0135	0.0150	0.0100	0.0110
3.....	2-hydroxy-4',4''-bis(dimethylamino)-triphenylmethane.....	5.7	7.5	0.52	0.95	0.0069	0.0069	0.0027	0.0026
4.....	4-hydroxy-3-methoxy-4',4''-bis-(dimethylamino)-triphenylmethane.....	12.3	18.1	-----	1.04	0.0064	0.0072	0.0061	0.0058
5.....	2-hydroxy-3-methoxy-4',4''-bis-(dimethylamino)-triphenylmethane.....	16.7	26.2	0.77	1.08	0.0100	0.0101	0.0051	0.0058
	None.....	145.5	360.0	3.87	4.97	0.0262	0.0426	1.0017	1.8461

Although Additive #1 is outstanding in its ability to inhibit oxidation as indicated by the low percentage increase in viscosity and also is outstanding in its ability to inhibit bearing loss, the compound has the disadvantage of being only slightly soluble in mineral oil at room temperature and, therefore, settles out. The compound is a good varnish inhibitor.

Additive #2 in which a methoxy group is substituted for an hydroxyl group in Additive #1, is also an excellent anti-oxidant and bearing corrosion inhibitor, but not so good as Additive #1. However, this additive is more soluble in mineral oil than Additive #1, one-half percent being readily soluble in the oil at room temperature. This compound is also a good varnish inhibitor.

Additive #3 differs from Additive #1 in that the hydroxyl group is attached to the phenyl ring in the position ortho to the central carbon atom of the molecule instead of para to the central carbon atom as in Additive #1. From the data in Table I it will be observed that this compound is an excellent anti-oxidant and corrosion inhibitor. It is also a good varnish inhibitor. It is readily soluble in mineral oil in amounts of one-half percent and greater at room temperature.

Additive #4 is similar to Additive #1 except that a methoxy group has been added to the phenyl ring in the meta position. The addition of the methoxy group serves to increase the solubility of this compound over that of Additive #1, although its solubility is not so good as Additives #2 and #3. From the data in Table I, it will be observed that the corrosion inhibiting and oxidation inhibiting properties of Additive #4 are midway between those of Additive #1 and Additive #2. Its varnish inhibiting characteristics are good.

In Additive #5 the methoxy group is in the same position as in Additive #4, but the hydroxyl

group has been changed to the ortho position. This compound is readily soluble in mineral lubricating oils and its oxidation inhibiting properties are very nearly the same as those of Additive #2, its bearing corrosion inhibiting properties are somewhat superior and its varnish inhibiting properties are excellent.

By comparing the results in Table I for oils containing additives with the results obtained on the oil containing no additives, it will be observed that each of the additives tested caused a marked lowering of viscosity increase, neutralization number and bearing loss.

In order to further demonstrate the oxidation inhibiting effect of additives falling within the scope of our invention, the same five additives tested and recorded in Table I were added to Mid-Continent neutral having a viscosity of 500 seconds Saybolt at 100° F. in the amount of .05 of to

0.5% and the several blends were subjected to a modified Davis oxygen-absorption test. The modified Davis absorption test is based on the method described in "Industrial & Engineering Chemistry," volume 33, page 339 (1941). In the test a ten gram sample is placed in a Sligh flask which is then filled with oxygen, connected to a U-type manometer and then placed in a constant temperature bath maintained at various selected temperatures. As oxygen is absorbed by the sample, pressure decreases in the flask and it is recorded at frequent intervals until it has dropped 60 mm. of mercury—the practical limit of the apparatus. The time required for the pressure drop of 60 mm. of mercury is taken as a measure of stability of the sample.

Iron naphthenate is added to the sample tested in order to catalyze the oxidation and accelerate the test.

The results of the test are recorded in Table II.

Table II

Number	Minutes to Drop 60 mm. in Pressure						
	Without Iron Naphthenate at—			With Iron Naphthenate in Following Amounts at 303° F.			
	275° F.	300° F.	350° F.	0%	0.0012%	0.012%	0.12%
1.....	2,160	1,240	275	1,240	1,460	1,310	840
2.....	3,380	1,620	305	1,620	2,640	1,730	265
3.....	1,860	1,030	420	1,080	780	860	860
4.....	7,200	2,730	375	2,730	2,480	2,490	1,210
5.....	4,670	2,800	370	2,800	2,570	2,660	1,220
None.....	2,380	1,078	156	1,078	940	149	93

It will be observed from a comparison of the tests in Table II of the sample containing Additive #1 and the sample containing no additive, that although Additive #1 does not exhibit any anti-oxidant activity at 275° F., it does exhibit anti-oxidant activity as the temperature in-

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creases. It will be further observed that the presence of iron naphthenate does not materially affect the anti-oxidant activity of Additive #1 at 300° F., whereas oxidation of the oil proceeds much more rapidly without additive as the amount of iron naphthenate present increases.

Additive #2 is more resistant to oxidation than is Additive #1 in the absence of iron naphthenate and in the presence of iron naphthenate up to amounts of .012%, but in the presence of .12% by weight its anti-oxidant effect is inferior to that of Additive #1.

Additive #3 follows somewhat the same pattern as Additive #1 in that its anti-oxidant effect at lower temperatures in the absence of iron naphthenate is poor, but improves at higher temperatures. Its anti-oxidant effect in the presence of iron naphthenate is excellent as shown by the fact that it is better with .12% of iron naphthenate than in the presence of .012%.

Additive #4 is remarkable for its anti-oxidant effect at lower temperatures in the absence of iron naphthenate. Its anti-oxidant effect in the presence of iron naphthenate is also remarkably good.

Additive #5 has substantially the same anti-oxidant effect as Additive #4, except that it is somewhat lower at 275° F. without iron naphthenate.

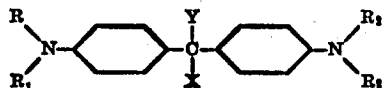
The data in the foregoing tables show that a hydroxyl group in the para position on the phenyl ring is in the most effective position from an oxidation inhibiting point of view, but that in this position the solubility of the compound is poor. The solubility of compounds having a hydroxyl group in the para position on the phenyl ring can be improved by incorporating in the ring an alkoxy group, preferably a methoxy group. By moving the hydroxyl group from the para to the ortho position, the solubility of the compound is greatly improved without materially lowering the oxidation inhibiting or other beneficial properties of the compound.

It is notable that during the second five-hour running on the Underwood test there was practically no bearing loss experienced in connection with any of the oils containing additives, whereas the mineral oil without additives showed a considerable bearing loss during the second five-hour running as well as during the first five hours.

Although the invention has been described with particular reference to use of additives in motor oils, it should be understood that the invention is applicable to the use of additives in compositions in general which are susceptible to undesirable oxidation in storage or during use, such as turbine oils, transformer oils, greases, quenching oils and other oils, fats and waxes, both hydrocarbon and non-hydrocarbon.

It is claimed:

1. A composition of matter comprising, a major portion of a hydrocarbon oil susceptible to oxidation and a compound in small amount effective to inhibit oxidation of said oil and having the formula



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where R, R₁, R₂ and R₃ are selected from the group consisting of hydrogen and alkyl groups, X is selected from the group consisting of hydrogen and a phenyl radical containing a substituent from the group consisting of amino and alkyl amino substituents in the position para to the central carbon atom of the molecule, and Y is a phenyl group containing a radical selected from the group consisting of hydroxyl and alkoxy groups.

2. A composition in accordance with claim 1 in which Y is a hydroxy phenyl ring.

3. A composition in accordance with claim 1 in which Y is a methoxy phenyl ring.

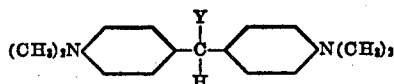
4. A composition in accordance with claim 1 in which Y is a phenyl ring containing a substituent of the group consisting of hydroxyl and methoxy groups.

5. A composition in accordance with claim 1 in which the compound is 2-hydroxy-4',4''-bis(dimethylamino)-triphenylmethane.

6. A composition in accordance with claim 1 in which the compound is 4-hydroxy-3-methoxy-4',4''-bis(dimethylamino)-triphenylmethane.

7. A composition in accordance with claim 1 in which the compound is 2-hydroxy-3-methoxy-4',4''-bis(dimethylamino)-triphenylmethane.

8. A lubricant comprising a major portion of mineral lubricating oil and approximately .01 to 5% by weight of a compound having the formula



where Y is a phenyl ring containing a radical selected from the group consisting of hydroxyl and alkoxy.

9. A lubricant in accordance with claim 8 in which the radical is hydroxyl.

10. A lubricant in accordance with claim 8 in which the radical is a hydroxyl group and the compound is 2-hydroxy-4',4''-bis(dimethylamino)-triphenylmethane.

11. A lubricant in accordance with claim 8 in which the phenyl ring contains an hydroxyl and a methoxy group.

12. A lubricant in accordance with claim 8 in which the compound is 2-hydroxy-3-methoxy-4',4''-bis(dimethylamino)-triphenylmethane.

13. A lubricant in accordance with claim 8 in which the compound is 4-hydroxy-3-methoxy-4',4''-bis(dimethylamino)-triphenylmethane.

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