Patented Aug. 30, 1949 2,480,450

UNITED STATES PATENT OFFICE

2,480,450

INHIBITING OXIDATION

Robert Cocroft and Elmer W. Brennan, Chicago, and Allan Manteuffel, Desplaines, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

No Drawing. Application July 19, 1945, Serial No. 606,020

13 Claims. (Cl. 252—47.5)

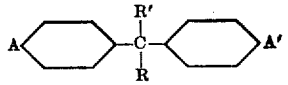
1

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.

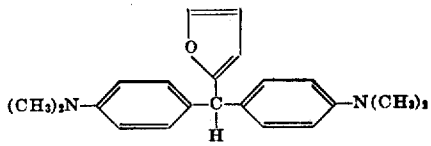
We have discovered that the effectiveness of compounds of the type above referred to in inhibiting oxidation of oxidizable lubricating liquids can be further improved as oxidation inhibitors and particularly with respect to inhibiting varnish formation by incorporating in the compound a heterocyclic ring attached to the central carbon atom of the molecule.

In accordance with our invention there is added to conventional hydrocarbon lubricating oils or to other compositions which are susceptible to undesirable oxidation in storage or during use, from approximately .01% or less up to 5% by weight, and preferably approximately 0.1 to 1% by weight of a compound having the following formula:



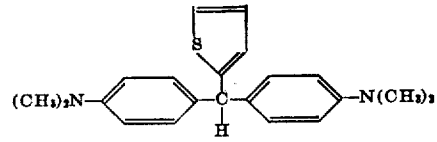
wherein A and A' are selected from the group consisting of amino, monoalkyl amino and dialkyl amino radicals, R is selected from the group consisting of hydrogen and a phenyl radical containing a substituent from the group consisting of amino, monoalkyl amino and dialkyl amino substituents in the position para to the central carbon atom of the molecule, and R' is a heterocyclic ring attached to the central carbon atom of the molecule by a carbon to carbon linkage.

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

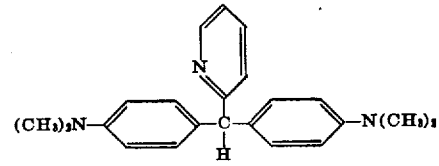


Bis-(4-dimethyl-aminophenyl)-2-furylmethane

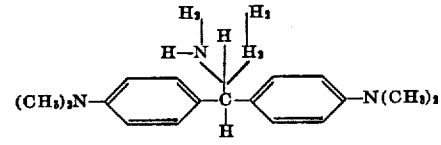
2



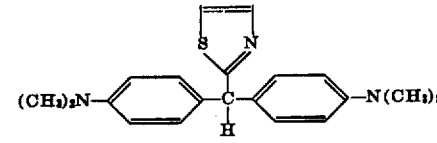
Bis-(4-dimethyl-aminophenyl)-2-thienylmethane



Bis-(4-dimethyl-aminophenyl)-2-pyridyl methane



Bis-(4-dimethyl-aminophenyl)-2-pyrolidyl methane



Bis-(4-dimethyl-aminophenyl)-2-thiazolyl-methane]

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 one test a Mid-Continent SAE 30 lubricating oil was tested without any additive. In another test 4,4'-bis-(dimethylamino)-diphenyl methane was added to the lubricating oil in amount of 0.5% by weight. This particular additive is a well-known commercial product which is marketed as a lubricating oil oxidation inhibi-

tor. In a third test the Mid-Continent SAE 30 lubricating oil had 0.5% by weight of bis-(4-dimethyl-aminophenyl)-2-furylmethane added to it. The Underwood tests were run at 325° F.

Iron naphthenate was added to some samples tested in order to catalyze the oxidation and accelerate the test.

The results of the test are recorded in Table II.

TABLE II

Davis oxygen absorption tests

Additive	Minutes Required for 60 mm. Drop in Pressure						
	Without Iron Naphthenate at			With Iron Naphthenate at 300° F. in amounts of—			
	275° F.	300° F.	350° F.	0% by wt.	0.0012% by wt.	0.012% by wt.	0.12% by wt.
None	2,380	1,078	156	1,078	940	149	93
4,4'-bis-(dimethylamino)-diphenyl methane	4,200	2,250	335	2,250	2,320	1,500	175
bis-(4-dimethylaminophenyl)-2-furylmethane	7,450	2,480	650	2,480	2,660	2,740	1,670

and at a pressure of ten pounds per square inch for a period of ten hours. The Underwood test is described in an article entitled "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

10 hour Underwood tests at 325° F.

Additive	Per Cent Increase in Viscosity at 130° F.		Neutralization No.		Bearing Loss in Grams			
					Cu-Pb		Ag-Cd	
	After 5 Hr.	After 10 Hr.	5 Hr.	10 Hr.	5 Hr.	10 Hr.	5 Hr.	10 Hr.
None	145.5	360.0	3.87	4.97	0.0262	0.0476	1.0017	1.8461
4, 4'-bis- (dimethylamino)-diphenylmethane	21.3	23.0	0.58	0.83	0.0036	0.0023	0.0255	0.0291
bis-(4-dimethylaminophenyl)-2-furylmethane	9.4	15.9	0.57	0.66	0.0067	0.0063	0.0123	0.0124

It is apparent from the results in Table I that not only did bis-(4-dimethyl-aminophenyl)-2-furylmethane greatly reduce the oxidation of the oil as indicated by the lower increase in viscosity and neutralization number and also greatly decrease bearing loss with respect to both copper-lead and silver-cadmium bearings, but this compound was noticeably superior to 4,4'-bis-(dimethylamino)-diphenyl methane which is regarded as one of the best commercial inhibitors available.

In order to further demonstrate the superior oxidation inhibiting ability of bis-(4-dimethyl-aminophenyl)-2-furylmethane, oxidation absorption tests in accordance with the modified Davis method were made on a Mid-Continent neutral oil having a viscosity of 500 S. U. S. at 100° F. and on this oil containing 0.5% of each of the two additives tested and recorded in Table I.

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.

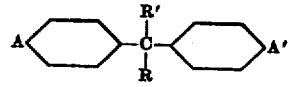
The results in Table II again demonstrate the superiority of bis-(4-dimethyl-aminophenyl)-2-furylmethane as an oxidation inhibitor. Its superiority is outstanding in connection with the test of the sample containing 0.12% by weight of iron naphthenate.

Although the specific examples show the heterocyclic ring as a single ring attached to the central carbon atom of the molecule at a point alpha to the hetero element, it is to be understood that the heterocyclic ring may be a condensed ring and that it may be attached to the central carbon atom of the molecule by means of a cyclic carbon atom in a position other than alpha to the hetero elements in the ring.

Although the invention has been described with particular reference to the use of additives in hydrocarbon lubricating oils it should be understood that the invention is applicable to use of additives in compositions in general, particularly liquid or semi-liquid, 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 in composition.

We claim:

1. A lubricant comprising mineral lubricating oil and a small amount, sufficient to inhibit oxidation of said oil, of a compound having the formula—



wherein A and A' are selected from the group consisting of amino, monoalkyl amino and dialkyl amino radicals, R is selected from the group consisting of hydrogen and a phenyl radical containing a substituent from the group consisting of amino, monoalkyl amino and dialkyl amino substituents in the position para to the central carbon atom of the molecule, and R' is a hetero-

cyclic ring attached to the central carbon atom of the molecule by a carbon to carbon linkage.

2. A lubricant in accordance with claim 1 in which A and A' are dimethylamino groups.

3. A lubricant in accordance with claim 1 in which A and A' are dimethylamino groups and R' is a furyl group.

4. A lubricant in accordance with claim 1 in which the compound is present in the composition in an amount of approximately .01 to 5% by weight.

5. A composition in accordance with claim 1 in which the compound is bis-(4-dimethyl-aminophenyl)-2-thienylmethane.

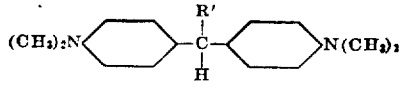
6. A composition in accordance with claim 1 in which the compound is bis-(4-dimethyl-aminophenyl)-2-pyridylmethane.

7. A composition in accordance with claim 1 in which the heterocyclic ring is one containing oxygen.

8. A composition in accordance with claim 1 in which the heterocyclic ring is one containing nitrogen.

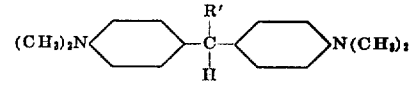
9. A composition in accordance with claim 1, in which the heterocyclic ring is one containing sulfur.

10. A lubricant comprising mineral lubricating oil, and a small amount, sufficient to inhibit oxidation of said oil, of a compound having the formula



in which R' is a heterocyclic ring attached to the central carbon atom of the molecule by a carbon to carbon linkage.

11. A composition from the group consisting of turbine oil, transformer oils, greases, quenching oils and lubricating oils comprising a mineral oil susceptible to oxidation and a small amount, sufficient to inhibit oxidation of said oil, of a compound having the formula



in which R' is a heterocyclic ring attached to the central carbon atom of the molecule by a carbon to carbon linkage.

12. A lubricant comprising mineral lubricating oil and a small amount, sufficient to inhibit oxidation of said oil, of bis-(4-dimethyl-aminophenyl)-2-furyl-methane.

13. A lubricant comprising mineral lubricating oil and approximately 0.1 to 1% by weight of bis-(4-dimethyl-amino-phenyl)-2-furyl-methane.

ROBERT COCROFT.
ELMER W. BRENNAN.
ALLAN MANTEUFFEL.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,000,045	Sloan	May 7, 1935