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# OXIDATION INHIBITORS FOR LUBRICATING OIL

George Oliver Pruett, Cos Cob, Conn., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

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9 Claims. (Cl. 252—51.5)

This invention relates to antioxidant compositions, to improve mineral oil lubricants containing the same and more particularly to improved mineral oil lubricants having increased resistance to oxidation whereby they are especially adapted for lubricating applications requiring good oxidation stability over extended periods of time without requiring extensive attention, service or maintenance.

In many lubricating applications, such as in the case of lubricants, coolants and rust preventatives for use in oil-circulating systems for steam-turbines, or as insulators and coolants for oil-filled transformers, circuit-breakers, switches, or the like, a very high degree of oxidation stability and an extended useful life is required inasmuch as it is desired that such uses be capable of undergoing extended periods of usage without involving attention, service or maintenance.

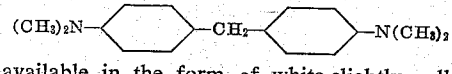
Many antioxidants or oxidation inhibitors are known and many of them have found widespread acceptance in industry. The requirements and demands on such antioxidants are such, however, that improvement thereon is a constant problem calling for continual advancement.

In some installations, higher concentrations of antioxidants in the lubricants have increased their oxidation prevention characteristics and extended their useful service lives but such efforts are expensive and uneconomical and are additionally limited by lubricant solubility for the antioxidant.

It is therefore a principal purpose of the present invention to provide an antioxidant composition adapted for use in low concentrations in a lubricant but nevertheless capable of markedly enhancing the oxidation stability of the lubricant over extended periods of time.

I have found that when 4,4'-tetramethyl diaminodiphenylmethane is used in conjunction with an antioxidant of the hindered phenolic type, a surprising synergistic action is realized whereby enormous increases in the oxidation stability of the lubricant are noted in the use of these materials collectively as contrasted to the expected properties anticipated from their individual characteristics.

4,4'-tetramethyl diaminodiphenylmethane (hereinafter sometimes referred to as MB) is an oxidation inhibitor and metal deactivator, is described in U. S. Patent 2,097,162, issued October 26, 1937, and possesses the following chemical structure:

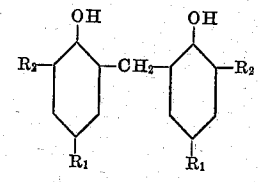



It is available in the form of white-slightly yellowish, odorless flakes, possesses a melting point of 87–98° C. (188.6–192.2° F.), contains less than 0.03% ash, less than 0.2% insolubles in benzene and less than 0.2% volatiles after 1 hour at 221° F.

Antioxidants of the hindered phenolic type are individually well known in the industry. The bis-phenolics, as more fully described in U. S. Patent 2,538,355, issued January 16, 1951, represent a large segment of such anti-

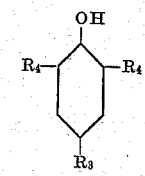


oxidants. They possess the following general chemical structure:




in which $R_1$ is an alkyl radical having from 1 to 3 carbon atoms, inclusive, and $R_2$ is a secondary or tertiary alkyl radical having up to 8 carbon atoms, inclusive, and preferably 4 to 8. Each $R_2$ is therefore joined to the aryl nucleus as an intermediate carbon atom.

The mono-phenolics, as more fully described in U. S. Patent 2,202,877, issued June 4, 1940, represents a second large segment of such antioxidants. They possess the following general chemical structure:




in which $R_3$ is an alkyl radical having up to 4 carbon atoms, inclusive, and $R_4$ is an alkyl radical having up to 8 carbon atoms, inclusive, but preferably 4 to 8.

Representative examples of $R_1$ include methyl, ethyl, propyl, and isopropyl; representative examples of $R_2$ include secondary butyl, tertiary butyl, tertiary amyl, tertiary octyl, etc.; representative examples of $R_3$ include methyl, ethyl, propyl, isopropyl, butyl, etc.; and illustrative examples of $R_4$ include methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, tertiary butyl, amyl, tertiary amyl, tertiary octyl, etc.

The concentrations of these antioxidants in the lubricant may vary widely with the contemplated usage, the nature and characteristics of the lubricant itself, etc. In normal operational applications, it has been found that combinations of from about 0.005 to about 0.2% by weight of MB and from about 0.005 to about 0.8% by weight of the hindered phenolic antioxidant yield the desired synergistic action.

Within the more commercial aspects of the present invention, however, it has been found that concentrations of MB of from about 0.01 to about 0.05% and from about 0.1 to about 0.4% of the hindered phenolic antioxidant are desirable.

If these materials are to be compounded into an antioxidant composition and sold for addition to the lubricant, such antioxidant composition should contain the individual components in such concentrations by parts as to yield the desired concentrations in the lubricant. That is to say, within the broader aspects from about 5 to about 200 parts of MB may be compounded with from about 5 parts to about 800 parts of the phenolic material. Within the more commercial aspects, however, from about 1 to about 5 parts of MB may be compounded with from about 1 to about 40 parts of the phenolic material.

These concentrations, as are all other concentrations referred to herein, are by weight based on the weight of the lubricant, unless otherwise specifically indicated.

The invention will be further illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples may describe in particular detail some of the more specific features of the present invention, they are given primarily for the purpose of illustration and the invention in its broader aspects is not to be construed as limited thereto.

## EXAMPLE 1

The synergistic effect in a Pennsylvania oil, a turbine oil base stock, SAE 20, 150 viscosity at 100° F., of a combination of MB and a mixture of hindered phenolic antioxidants derived from the reaction of an alkylated p-cresol (or homologue thereof) and formaldehyde (hereinafter sometimes referred to as 123), more fully described in copending application Serial Number 382,210, filed September 24, 1953, was determined by means of an A. S. T. M. test D943–47T (oxidation characteristics of inhibited steam-turbine oils), as set forth in A. S. T. M. standards, 1952, part 5, pages 409–413.

*Table 1*

| Additive | Concentration, percent | Induction Period, hours |
|---|---|---|
| MB | 0.05 | 72 |
| 123 | 0.4 | 1,510 |

A combination of 0.025% MB and 0.2% 123 was calculated to yield an anticipated induction period of 791 hours. Actually, an induction period of 2784 hours was obtained in the test. Thus, even though the concentrations were halved, the induction period of the combination was vastly increased over the sum of the individual induction periods obtained by the separate use of the components at double strength.

In the following examples, a test for determining the induction period of the lubricant in question is referred to as a means of establishing resistance to oxidation.

The test is carried out as follows: 300 grams of the oil is weighed out and to it is added an amount of each additive to bring that additive content up to the value indicated. The mixture is then placed in a cylindrical glass vessel of 40 cm. diameter and 400 cm. height with a fritted glass air-inlet tube at the bottom and an exit gas tube at the top. The vessel is then placed in a thermostated bath controlled at 155° C. and pure nitrogen is bubbled through the solution at 200 cc. per minute for 1 hour, during which time the solution reaches the bath temperature. The gas stream is then switched to air at 200 cc. per minute and the time noted. The outlet gas stream is then passed through a paramagnetic type oxygen analyzer, where its oxygen content is measured and recorded as a function of time. The time at which the solution begins to absorb oxygen is noted by the rapid drop in the oxygen content of the outlet gas stream. This time can be determined very accurately and is recorded in the tables as the "induction period," being the number of hours elapsed between the switch from nitrogen to air, and the rapid drop in the oxygen content of the outlet gas stream.

## EXAMPLE 2

The synergistic effect of a combination of MB and 2,2'-methylenebis(4-ethyl-6-tert. butylphenol) (herein sometimes referred to as 425) was determined as follows:

*Table 2*

| Additive | Concentration, percent | Induction Period, hours |
|---|---|---|
| MB alone | 0.02 | 1.7 |
| 425 alone | 0.02 | 46.8 |

A combination of 0.01% MB and 0.01% 425 was calculated to yield an anticipated induction period of 24.3 hours. Actually, an induction period of 36.7 hours was obtained in the test.

A combination of 0.02% MB and 0.02% 425 was calculated to yield an anticipated induction period of 48.5 hours. Actually, an induction period of 72.0 hours was obtained in the test.



## EXAMPLE 3

The synergistic effect of a combination of MB and 2,2'-methylenebis(4-methyl-6 tert. butylphenol) (herein sometimes referred to as 2246) was determined as follows:

*Table 3*

| Additive | Concentration, percent | Induction Period, hours |
|---|---|---|
| MB alone | 0.02 | 1.7 |
| 2246 alone | 0.02 | 54.1 |

A combination of 0.01% MB and 0.01% 2246 was calculated to yield an anticipated induction period of 27.9 hours. Actually, an induction period of 38 hours was obtained in the test.

A combination of 0.02% MB and 0.02% 2246 was calculated to yield an anticipated induction period of 55.8 hours. Actually, an induction period of 76.0 hours was obtained in the test.

## EXAMPLE 4

The synergistic effect of a combination of MB and 2,6-ditert-butyl-4-methylphenol (hereinafter sometimes refered to as I) was determined as follows:

*Table 4*

| Additive | Concentration, percent | Induction Period, hours |
|---|---|---|
| MB alone | 0.02 | 1.7 |
| I alone | 0.02 | 15.5 |

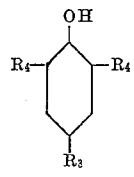
A combination of 0.01% MB and 0.01% I was calculated to yield an anticipated induction period of 8.6 hours. Actually, an induction period of 9.8 hours was obtained in the test.

A combination of 0.02% MB and 0.02% I was calculated to yield an anticipated induction period of 17.2 hours. Actually, an induction period of 19.9 hours was obtained in the test.

Although I have described specific examples of my inventive concept, I consider the broad aspects of the same not to be limited to the specific substances mentioned therein but to include various other compounds of equivalent function and constitution as set forth in the claims appended hereto. It is understood that any suitable changes, modifications and variations may be made without departing from the spirit and scope of the invention.

**I claim:**

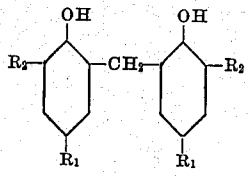
1. An antioxidant composition for mineral oil lubricants comprising from about 1 to about 5 parts of 4,4'-tetramethyl diaminodiphenylmethane and from about 1 to about 40 parts of an antioxidant of the hindered monophenol type having the formula




wherein $R_3$ is an alkyl radical having from 1 to 4 carbon atoms and $R_4$ is an alkyl radical having up to 8 carbon atoms.

2. An antioxidant composition for mineral oil lubricants comprising from about 1 to about 5 parts of 4,4'-tetramethyl diaminodiphenylmethane and from about 1 to

about 40 parts of an antioxidant of the hindered bis-phenolic type having the formula



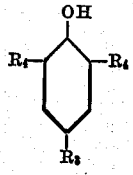
wherein $R_1$ is an alkyl radical having from 1 to 3 carbon atoms and $R_2$ is a member of the group consisting of secondary and tertiary alkyl radicals having up to 8 carbon atoms.

3. An antioxidant composition as defined in claim 1 wherein the hindered mono-phenolic antioxidant is 2,6-di-tertiary-butyl-4-methylphenol.

4. An antioxidant composition as defined in claim 2 wherein the hindered bis-phenolic antioxidant is 2,2'-methylenebis-(4-ethyl-6-tertiary butylphenol).

5. A lubricating oil composition comprising a major portion of a mineral lubricating oil and a minor portion of an antioxidant composition comprising from about 0.01 to about 0.05% of 4,4'-tetramethyl diaminodiphenylmethane and from about 0.01 to about 0.4% of an antioxidant of the hindered phenolic type from the group consisting of 2,4,6-trialkylphenol wherein the alkyl groups at the 2 and 6 positions contain from 1 to 4 carbon atoms and the alkyl group at the 4 position contains up to 8 carbon atoms and 2,2'-methylenebis(4,6-dialkylphenol) wherein the alkyl group at the 4 position contains from 1 to 3 carbon atoms and the alkyl group at the 6 position is a member of the group consisting of secondary and tertiary alkyl groups containing up to 8 carbon atoms, said percentages being by weight based on the weight of the lubricating oil.

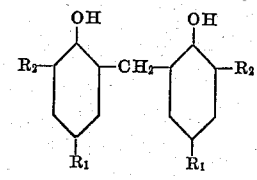
6. A lubricating oil composition comprising a major portion of a mineral lubricating oil and a minor portion of an antioxidant composition comprising from about 0.01 to about 0.05% of 4,4'-tetramethyl diaminodiphenylmethane and from about 0.01 to about 0.4% of an antioxidant of the hindered mono-phenolic type having the formula



wherein $R_3$ is an alkyl radical having from 1 to 4 carbon atoms and $R_4$ is an alkyl radical having up to about 8 carbon atoms, said percentages being by weight based on the weight of the lubricating oil.



7. A lubricating oil composition comprising a major portion of a mineral lubricating oil and a minor portion of an antioxidant composition comprising from about 0.01 to about 0.05% of 4,4'-tetramethyl diaminodiphenylmethane and from about 0.01 to about 0.4% of an antioxidant of the hindered bis-phenolic type having the formula



wherein $R_1$ is an alkyl radical having from 1 to 3 carbon atoms and $R_2$ is a member of the group consisting of secondary and tertiary alkyl radicals having up to 8 carbon atoms, said percentages being by weight based on the weight of the lubricating oil.

8. An antioxidant composition for mineral oil lubricants comprising about 1 part of 4,4'-tetramethyl diaminodiphenylmethane and from about 1 part to about 8 parts of an antioxidant of the hindered phenolic type from the group consisting of 2,4,6-trialkylphenol wherein the alkyl groups at the 2 and 6 positions contain from 1 to 4 carbon atoms and the alkyl group at the 4 position contains up to 8 carbon atoms and 2,2'-methylenebis(4,6-dialkylphenol) wherein the alkyl group at the 4 position contains from 1 to 3 carbon atoms and the alkyl group at the 6 position is a member of the group consisting of secondary and tertiary alkyl groups containing up to 8 carbon atoms.

9. An antioxidant composition for mineral oil lubricants comprising from about 1 to about 5 parts of 4.4'-tetramethyldiaminodiphenylmethane and from about 1 to about 40 parts of an antioxidant of the hindered phenolic type selected from the group consisting of 2,4,6-trialkylphenols wherein the alkyl groups at the 2 and 6 positions contain from 1 to 8 carbon atoms and the alkyl group at the 4 position contain from 1 to 4 carbon atoms and 2,2-methylene bis-(4,6-dialkylphenol) wherein the alkyl groups at the 4 positions contain from 1 to 3 carbon atoms and the alkyl group at each 6 position is joined thereto at an intermediate carbon atom and contains up to 8 carbon atoms.


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