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STABILIZED MINERAL OIL LUBRICANT COMPOSITIONS

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This invention relates to stabilized mineral oil lubricant compositions, and more particularly, it relates to mineral oil lubricants which have been stabilized against oxidative deterioration. More specifically, this invention is concerned with improvements in mineral lubricant compositions containing addition agents of the type disclosed in the copending application of Smith, Cantrell and Peters, Serial No. 772,014, filed September 3, 1947, now U. S. Patent No. 2,504,742.

Plain mineral lubricating oils often prove unsatisfactory in the lubrication of internal combustion engines of all types, particularly when severe operating conditions are encountered, because of the oxidative deterioration of the oil with the attendant deposition on the engine surfaces of varnish, gum or sludge. Furthermore, many lubricating oil compositions which may be satisfactory for the lubrication of other mechanisms have been found wholly unsuitable for use as turbine oils.

The formation of varnishes, gums and sludges on engine surfaces is generally ascribed, at least in part, to oxidation effects on mineral lubricating oils. The problem of oxidation is further aggravated in turbine oils because in normal use turbine oils become rapidly contaminated with water.

While the type of additive disclosed and claimed in copending application, Serial No. 772,014, confers a remarkably effective oxidation stability on mineral lubricating oils, the oils in use sometimes acquire a dark color albeit their oxidation stability remains generally unimpaired. This darkening in color, although insignificant from the standpoint of oxidation stability, is important from the standpoint of the consumer, because to him, the darkening in color during use of the oil would normally be indicative of degradation, whether or not that is the fact. It would be advantageous, therefore, to provide mineral lubricating oils which remain light in color even after extended periods of use.

The principal object of this invention, then, is to provide mineral oil lubricant compositions which, in addition to being stabilized against oxidative deterioration, will not materially be darkened in color during use. Other objects will be apparent from the following detailed description.

The objects are accomplished by the present invention which resides in the provision of a mineral lubricating oil containing (1) 2,6-ditertiarybutyl-4-methyl phenol and (2) a non-resinous condensation product of from 1 to 4 mols of a monohydric phenol having at least one unsubstituted nuclear position, 1 to 4 mols of N-dimethylaniline and 0.5 to 4 mols of formaldehyde per mol of the phenol, the condensation having been carried out in the presence of an activated clay catalyst at a temperature not in excess of 350° F. to condense together the three reactants.

We have found that when a mineral lubricating oil is stabilized against oxidative deterioration by the use of both of the additives set forth herein, darkening of the mineral lubricating oil in use is materially retarded. We have also found that within proportions of about 0.5 per cent by weight total additive, the two additives unexpectedly synergize each other; that is, the antioxidant life of a mineral oil containing both additives is greater than the sum of the antioxidant effects obtained from the use of the individual additives alone.

As disclosed in U. S. Patent No. 2,265,582, 2,6-ditertiarybutyl-4-methyl phenol is by itself a good antioxidant. As disclosed in copending application Serial No. 772,014,

the non-resinous phenol - dimethylaniline - formaldehyde condensation product prepared in the presence of an activated clay is in itself an excellent antioxidant, it being generally more potent than 2,6-ditertiarybutyl-4-methyl phenol, particularly under service conditions involving high temperatures. Our invention resides in using both of these antioxidants in one mineral lubricating oil to obtain as new and unexpected results the stabilization of the color of the oil during use and a synergistic effect on oxidation stability of the oil when the sum of the amounts of both additives does not exceed about 0.5 per cent by weight of the oil.

As disclosed in copending application Serial No. 772,014, the non-resinous phenol-dimethylaniline-formaldehyde condensation product is prepared by heating the reactants in the presence of an activated clay catalyst at a temperature not in excess of 350° F. to condense together the three reactants. We have found that if the temperature of 350° F. is exceeded to any substantial extent, the condensation product formed tends to be resinous and insoluble. The preferred temperature for the condensation ranges from 150° to 300° F. The proportions of the reactants used to prepare the condensation product vary over a relatively wide range. The monohydric phenol is employed in an amount of from 1 to 4 mols; N-dimethylaniline is employed in an amount of from 1 to 4 mols; and the amount of formaldehyde ranges from 0.5 to 4 mols of formaldehyde per mol of the phenol. Ordinarily it is preferred to use from 5 to 10 per cent by weight of an activated clay catalyst based on the total weight of the reactants. However, smaller amounts, as low as 1 per cent by weight, and larger amounts, as high as 20 per cent by weight, can be used; but larger amounts than about 10 per cent by weight are ordinarily not necessary. Contrary to what may be expected from the nature of the reactants, we do not obtain highly condensed, insoluble resinous products. On the contrary, when the above reactants are condensed in accordance with our copending application above referred to, there are obtained light-colored condensation products which are non-resinous and which are readily soluble in mineral oils.

The monohydric phenols which are used in the condensation reaction to form the condensation products include phenol itself and the substituted monohydric phenols having at least one unsubstituted nuclear position. Among the substituted phenols, we prefer to use the alkylated monohydric phenols, including mono- and polyalkylated phenols, such as ortho, meta and para cresols and mixtures thereof, e. g., cresylic acid, the various xylenols, ortho, meta and para ethyl phenol, para propyl and isopropyl phenols, phlorol, ortho and para tertiarybutyl phenol, 2,4-ditertiarybutyl phenol, 2,4,6-tritertiarylbutyl phenol, ortho and para tertiaryamyl phenol, tritertiaryamyl phenol hexyl phenols, heptyl phenols, octyl phenols, hexadecyl phenol, octadecyl phenol, thymol, carvacrol, mesitol (2,4,6-trimethyl phenol), durenol (1,2,4,5-tetramethyl-3-hydroxybenzene) and the like. Para cresol and octyl (paratetramethylbutyl) phenol are advantageously used. Other substituted phenols which we employ include alkoxy phenols and mixed alphyl, alkoxy phenols, such as guaiacol, chavibetol, eugenol, isoeugenol and cresol. In addition, polynuclear monohydric phenols such as alpha and beta naphthols, anthrols, phenanthrols, pyrenol, and the like are also advantageously employed. Other substituted phenols than alkyl, alkenyl, aryl and alkoxy phenols are also suitable. These include the halo, nitro, amino and alkylamino phenols, and the like. Examples of such phenols are ortho and para chlorophenol, 2-nitro-4-amino phenol, para amino phenol, para dimethylamino phenol, etc. It will be seen, therefore, that the term "monohydric phenol having at least one unsubstituted nuclear position" includes both substituted and unsubstituted monohydric phenols which are either monocyclic or polynuclear.

In lieu of formaldehyde in the condensation reaction, any formaldehyde-yielding compound can be used, such as paraformaldehyde, dioxymethylene and trioxymethylene. In such case, the amount of formaldehyde-yielding compound used is based on the equivalent number of

mols of formaldehyde yielded within the range of proportions of formaldehyde set forth hereinabove. Accordingly, as used in the appended claims, the term "formaldehyde" is intended to include formaldehyde-yielding compounds as well as formaldehyde itself.

Various activated clay catalysts are employed in the preparation of the phenol-dimethylaniline-formaldehyde condensation product. Such materials are well known in the art and comprise a natural clay, such as bentonite, fuller's earth, floridin and smectite, which has been acid treated in order to activate the clay. These materials are described in U. S. Patent No. 1,898,165, for example.

In preparing the phenol-dimethylaniline-formaldehyde condensation product, the reactants and catalyst are placed in a reaction vessel which is then closed and the mixture heated with agitation until all of the formaldehyde or formaldehyde-yielding compound has been consumed. At this time the water which is formed as a result of the condensation is removed, preferably under vacuum, and the dehydrated condensation product is then filtered to remove the activated clay catalyst. If it is desired, the condensation product may be prepared in a concentrate in a mineral lubricating oil which may then be diluted with additional oil to the final concentration desired. These condensation products are liquids or crystalline solids and contain in combination all three of the reactants employed in their preparation. As shown in the copending application hereinabove referred to, the use of an activated clay as a catalyst is essential in the preparation of the condensation products; otherwise black, insoluble, resinous condensation products are obtained.

The other agent, 2,6-ditertiarybutyl-4-methyl phenol, which we employ in the lubricants of this invention, may be obtained from any suitable source. One method of preparing 2,6-ditertiary-butyl-4-methyl phenol is disclosed in U. S. Patent No. 2,265,582 and comprises alkylating para cresol with isobutylene until no more isobutylene reacts with the para cresol.

For the purposes of the present invention, the phenol-dimethylaniline-formaldehyde condensation product and 2,6-ditertiarybutyl-4-methyl phenol are added to mineral lubricating oils in minor amounts, say in a total amount of both additives of from 0.01 to 1.0 per cent by weight on the mineral oil, sufficient to inhibit oxidative deterioration of the oil. Larger amounts of our additives may be used if desired, but it is ordinarily unnecessary to do so. Within the total amounts of both additives set forth herein, each additive may range from 20 to 80 per cent by weight of the total, i. e., in a weight ratio of from 1:4 to 4:1. Stated in another way, in order to obtain the desired results as to retardation of darkening in color, at least 20 per cent by weight of the total additives should be 2,6-ditertiary-butyl-4-methyl phenol; and in order to obtain the beneficial effects of the condensation product in prolonging oxidation stability, at least 20 per cent by weight of the total additives should be phenol-dimethylaniline-formaldehyde condensation product. While the color retardation effect of our invention is obtained over the whole range of proportions of total additive disclosed herein, the additional synergistic effect of the two additives on each other as hereinabove disclosed, is obtained only when the total amount of additive does not exceed about 0.5 per cent by weight of the oil. Above this amount, the antioxidant effects of the two additives tend to be cumulative rather than synergistic. It is understood, of course, that in the synergistic range also, each additive is present in an amount of at least 20 per cent of the total additive employed.

The following examples are illustrative of our invention. The oxidation test referred to therein is a standard test designated ASTM D 943–47 T. Briefly, the test comprises subjecting the oil sample to oxygen at a temperature of 95° C. (203° F.) in the presence of water and an iron-copper catalyst, and determining the time required to build up a neutralization number of 2.0. The flow of oxygen is maintained at 3 liters per hour. The remarkably effective stability to oxidation of the mineral oil lubricant compositions containing our new addition agents, the color improvements and the synergistic effects are illustrated by the results shown in the following examples:

Example I.—A portion of turbine oil stock was treated

with 0.2 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol, and another portion of this stock was treated with 0.2 per cent by weight of (B) the condensation product of 1 mol of octyl (paratetramethylbutyl) phenol, 4 mols of N-dimethylaniline and 4 mols of formaldehyde, prepared in the presence of 10 per cent by weight of Filtrol (activated clay) under the conditions disclosed hereinabove. A third portion was treated with both 0.2 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol and 0.2 per cent by weight of (B) the condensation product of octyl phenol, N-dimethylaniline and formaldehyde. The base oil, the oil blended with (A), the oil blended with (B), ad the oil blended with both (A) and (B) exhibited the following properties:

	Base Oil	Base Oil Containing 0.2% of (A)	Base Oil Containing 0.2% of (B)	Base Oil Containing 0.2% of (A) and 0.2% of (B)
Gravity, ° API	28.5	28.4	28.4	28.3
Viscosity, SUV, 100° F	610	611	610	612
Flash, OC, ° F	490	490	490	490
Pour, ° F	+5	+5	+5	+5
Color, NPA	2.5	2.5	2.5	2.5
Oxidation Test, ASTM D943–47T:				
Time Oxidized, Hrs	219	400	1,400	2,450
Neutralization No	2.0	2.0	2.0	2.0
Expected Time Oxidized, Hrs				1,800
Increase Over Expected Time Oxidized, Hrs				650
Color of Oxidized Oil after 14 Days' Oxidation Test, NPA	5.0	2.5	4.5	2.5

Example II.—A portion of turbine oil stock was treated with 0.1 per cent by weight of (A) 2,6-ditertiary-butyl-4-methyl phenol, and another portion of this stock was treated with 0.1 per cent by weight of (B) the condensation product of 1 mol octyl (paratetramethylbutyl) phenol, 4 mols N-dimethylaniline and 4 mols of formaldehyde. A third portion was treated with both 0.1 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol and 0.1 per cent by weight of (B) the condensation product of octyl phenol, N-dimethylaniline and formaldehyde. The base oil, the oil blended with (A), the oil blended with (B), and the oil blended with both (A) and (B) showed the following results:

	Base Oil	Base Oil Containing 0.1% of (A)	Base Oil Containing 0.1% of (B)	Base Oil Containing 0.1% of (A) and 0.1% of (B)
Color, NPA	1.5	1.5	1.5	1.5
Oxidation Test, ASTM D943–47T:				
Time Oxidized, Hrs	195	280	370	750
Neutralization No	2.0	2.0	2.0	2.0
Expected Time Oxidized, Hrs				650
Increase Over Expected Time Oxidized, Hrs				100
Color of Oil After 14 Days' Oxidation Test, NPA	5.0	2.0	5.0	2.0

Example III.—A portion of turbine oil stock was treated with 0.3 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol, and another portion of this stock was treated with 0.3 per cent by weight of (B) the condensation product of 1 mol octyl (paratetramethylbutyl) phenol, 4 mols of N-dimethylaniline and 4 mols of formaldehyde. A third portion was treated with both 0.3 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol and 0.3 per cent by weight of (B) the condensation product of octyl phenol, N-dimethylaniline and formaldehyde. The base oil, the oil blended with (A),

the oil blended with (B), and the oil blended with both (A) and (B) showed the following results:

	Base Oil	Base Oil Containing 0.3% of (A)	Base Oil Containing 0.3% of (B)	Base Oil Containing 0.3% of (A) and 0.3% of (B)
Color, NPA	1.5	1.5	1.5	1.5
Oxidation Test, ASTM D943-47T:				
Time Oxidized, Hrs	195	600	3,500	4,000
Neutralization No	2.0	2.0	2.0	2.0
Expected Time Oxidized, Hrs				4,100
Increase Over Expected Time Oxidized, Hrs				(−100)
Color of Oil After 14 Days' Oxidation Test, NPA	5.0	2.0	5.0	2.0

Example IV.—A portion of turbine oil stock was treated with 0.2 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol, and another portion of this stock was treated with 0.2 per cent by weight of (B) the condensation product of 1 mol of para cresol, 2 mols of N-dimethylaniline and 2 mols of formaldehyde in the presence of Filtrol activated clay prepared under the conditions disclosed hereinabove. A third portion was treated with both 0.2 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol and 0.2 per cent by weight of (B) the condensation product of para cresol, N-dimethylaniline and formaldehyde. The base oil, the oil blended with (A), the oil blended with (B), and the oil blended with both (A) and (B) showed the following results:

	Base Oil	Base Oil Containing 0.2% of (A)	Base Oil Containing 0.2% of (B)	Base Oil Containing 0.2% of (A) and 0.2% of (B)
Gravity, °API	28.8	28.7	28.7	28.7
Viscosity, SUV, 100° F	303	301	301	302
Oxidation Test, ASTM D943-47T:				
Time Oxidized, Hrs	85	350	865	1,550
Neutralization No	2.0	2.0	2.0	2.0
Expected Time Oxidized, Hrs				1,215
Increase Over Expected Time Oxidized, Hrs				335
Color of Oil After 14 Days' Oxidation Test, NPA	8.0	2.0	8.0	2.0

Example V.—A portion of turbine oil stock was treated with 0.1 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol and another portion of this stock was treated with 0.3 per cent by weight of (B), the condensation product of 1 mol of para cresol, 2 mols of N-dimethylaniline and 2 mols of formaldehyde, prepared in the presence of 10 per cent by weight of Filtrol. A third portion of the turbine oil stock was treated with both 0.1 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol and 0.3 per cent by weight of (B) the condensation product of para cresol, N-dimethylaniline and formaldehyde. The base oil, the oil blended with (A), the oil blended with (B), and the oil blended with both (A) and (B) showed the following results:

	Base Oil	Base Oil Containing 0.1% of (A)	Base Oil Containing 0.3% of (B)	Base Oil Containing 0.1% of (A) and 0.3% of (B)
Oxidation Test, ASTM D943-47T:				
Time Oxidized, Hrs	195	280	3,500	4,000
Neutralization No	2.0	2.0	2.0	2.0
Expected Time Oxidized, Hrs				3,780
Increase Over Expected Time Oxidized, Hrs				220
Color of Oil After 14 Days' Oxidation Test, NPA	5.0	2.0	5.0	2.0

Example VI.—A portion of turbine oil stock was treated with 0.3 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol and another portion of this stock was treated with 0.1 per cent by weight of (B) the condensation product of 1 mol of para cresol, 2 mols of N-dimethylaniline and 2 mols of formaldehyde, prepared in the presence of Filtrol. A third portion was treated with both 0.3 per cent by weight of (A) 2,6-ditertiarybutyl-4-methyl phenol and (B) 0.1 per cent by weight of the condensation product of para cresol, N-dimethylaniline and formaldehyde. The base oil, the oil blended with (A), the oil blended with (B), and the oil blended with both (A) and (B) showed the following results:

	Base Oil	Base Oil Containing 0.3% of (A)	Base Oil Containing 0.1% of (B)	Base Oil Containing 0.3% of (A) and 0.1% of (B)
Oxidation Test, ASTM D943-47T:				
Time Oxidized, Hrs	195	600	370	1,250
Neutralization No	2.0	2.0	2.0	2.0
Expected Time Oxidized, Hrs				970
Increase Over Expected Time Oxidized, Hrs				280
Color of Oil After 14 Days' Oxidation Test, NPA	5.0	2.0	5.0	2.0

The preceding examples clearly illustrate the remarkable properties of our new mineral oil lubricant compositions. The color tests made during oxidation show that the base oil and the oil containing the phenol-dimethylaniline-formaldehyde condensation products alone turned dark during oxidation, while the oil containing both additives in accordance with the present invention retained its pristine color. The color test referred to is described in "ASTM Standards on Petroleum Products and Lubricants," November 1948, pages 105–109 (ASTM D 155–45 T). A National Petroleum Association (NPA) color number of 2 designates an oil slightly darker than "cream white," namely "extra pale." Also significant is the fact that while the lubricating oil containing the phenol-dimethylaniline-formaldehyde condensation products alone turned dark during oxidation, only a small amount of 2,6-ditertiary-butyl-4-methyl phenol need be added to give an NPA color of 2. Thus, a base oil containing 0.3 per cent by weight on the oil of the condensation product of octyl phenol, N-dimethylaniline and formaldehyde will turn dark during oxidation; but if only 0.1 per cent by weight on the oil of 2,6-ditertiary-butyl-4-methyl phenol is added, the oil will not turn dark.

In addition to color improvement, the above examples clearly show the unexpected synergistic effect with respect to antioxidant potency when the total amount of the two additives does not exceed about 0.5 per cent by weight on the mineral oil. In preceding Example I, for instance, the lubricating oil containing the combination of ingredients was much more stable to oxidation than oils containing the ingredients separately. The oil containing only 2,6-ditertiarybutyl-4-methyl phenol had an antioxidant life of 400 hours. The oil containing only the phenol-dimethylaniline-formaldehyde condensation product had an antioxidant life of 1400 hours. It would be expected, therefore, that an oil containing both ingredients would have an antioxidant life of about 1800 hours. However, the test shows that the improved oil of this invention had an antioxidant life of 2450 hours, indicating an unexpected synergistic effect.

The above examples also show the remarkable oxidation stability imparted to mineral oil lubricant compositions by the use of our new addition agents. Mineral oil lubricant compositions containing our new addition agents are therefore eminently suited for use where the operating conditions are extremely severe, as in diesel, tank and truck engines, and in the lubrication of steam turbines. Furthermore, the beneficial effects of our invention may be applied to all types of lubricating oil base stocks, that is, paraffinic, naphthenic and mixed base stocks.

If desired, other known addition agents may be incorporated into the lubricant composition prepared in accordance with our invention. For example, pour point

depressants, extreme-pressure agents, and the like may be added. Resort may be had to such modifications and variations as fall within the spirit of the invention and the scope of the appended claims.

We claim:

1. A lubricant composition comprising a major amount of a mineral lubricating oil and minor amounts, in a total of from 0.01 to 1 per cent by weight of said oil of: (1) 2,6-ditertiarybutyl-4-methyl phenol; and (2) a non-resinous condensation product of 1 mol of paratetramethylbutyl phenol, 4 mols of N-dimethylaniline and 4 mols of formaldehyde, the condensation of said product having been carried out in the presence of from 5 to 10 per cent by weight on the reactants of an activated clay catalyst at a temperature of from 150° to 300° F. to condense together the three reactants; the amounts of (1) and (2) with respect to each other being in a weight ratio ranging from 1:4 to 4:1.

2. The composition of claim 1, wherein each of the compounds (1) and (2) is present in an amount of 0.2 per cent by weight.

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