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ANTIOXIDANTS FOR MINERAL OIL LUBRICANTS AND COMPOSITIONS CONTAINING THE SAME

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This invention relates to antioxidants for mineral oil lubricants and compositions containing the same, and more particularly, it relates to addition agents for mineral oil lubricants which inhibit the oxidative deterioration of said lubricants.

In the lubrication of internal combustion engines of all types, particularly when severe operating conditions are encountered, plain mineral lubricating oils often prove unsatisfactory in service 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 highly 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 due at least in part to oxidation effect on mineral lubricating oils. In turbine oils the problem of oxidation is further aggravated, because in normal use turbine oils rapidly become contaminated with water.

It is an object of this invention, therefore, to provide an addition agent for mineral oil lubricants which will inhibit the oxidative deterioration of such lubricants.

It is further an object of this invention to provide mineral oil lubricant compositions which are remarkably stable against oxidation under service conditions.

These and other objects are accomplished by the present invention wherein an addition agent for mineral oil lubricants is prepared by condensing phenothiazine, N-dimethylaniline and formaldehyde in the presence of an activated clay as a catalyst, and neutralizing the condensation product with cyclohexylamine. The product so obtained is a light-colored product which, when added to mineral oil lubricants, confers a remarkable stability against deterioration by oxidation. Such products and mineral oil lubricant compositions containing them are believed to be novel and are considered parts of our invention. 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 and neutralized in accordance with our invention, there are obtained light-colored products which are non-resinous and which are readily soluble in mineral oils.

In performing the condensation the reactants

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are mixed and heated to a maximum temperature of 350° F. We have found that if the temperature of 350° F. is exceeded to any substantial extent, the neutralized condensation product tends to be resinous and insoluble. In general, the preferred temperature for the condensation ranges from 150° to 300° F. The neutralization occurs upon mere mixing of the condensation product and the cyclohexylamine, but mildly elevated temperatures, say 80° F. to 200° F. can be employed.

The proportions of the reactants vary over a relatively wide range. For each mol of phenothiazine, N-dimethylaniline is employed in an amount of from 4 to 9 mols, and the formaldehyde is employed in an amount from 4 to 9 mols. The cyclohexylamine is employed in an amount sufficient to give a substantially neutral product.

Ordinarily, it is preferred to use from 5 to 10 per cent by weight of the 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, may also be employed; but larger amounts than about 10 per cent by weight are ordinarily not necessary.

As stated, the condensation product of phenothiazine, N-dimethylaniline and formaldehyde as prepared in accordance with the above disclosure is neutralized with cyclohexylamine. When so neutralized, it is readily soluble in mineral lubricating oils and confers excellent antioxidant stability thereto.

In lieu of formaldehyde any formaldehyde-yielding compound, such as paraformaldehyde, dioxymethylene and trioxymethylene may be employed. 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 clays are employed as catalysts in accordance with our invention. Such materials are well known in the art and comprise a natural clay, such as bentonite, montmorillonite, 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 1,898,165, for example.

In preparing our new addition agents, the re-

actants to be condensed and the catalyst are placed into a reaction vessel which is then closed and the mixture heated with agitation under reflux 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. The product is then neutralized with cyclohexylamine. In some instances, it is desirable to prepare our new addition agent as a concentrate in a mineral lubricating oil which may then be diluted with additional oil to the concentration desired in the final lubricating composition. In such instances, the mineral lubricating oil may be added in a suitable amount, say in a weight equal to the weight of reactants, to the reaction mixture in the reaction vessel, and after neutralization the product obtained will then be a concentrated solution of the addition agent in the mineral lubricating oil.

The products obtained in accordance with our invention are liquids or crystalline solids. While the exact nature of the chemical composition of the condensation products is unknown, all of the three condensation reactants enter into a final unitary product. The exact nature of the manner in which the catalyst influences the reaction is unknown. However, regardless of any theory involved, the use of an activated clay catalyst is an essential feature of our invention, since if the catalyst is omitted, black, insoluble, resinous condensation products are obtained.

The following examples illustrate the preparation of our new addition agent.

Example I.—Into an enamel-lined reaction vessel were charged 199 parts by weight of phenothiazine (1 mol), 605 parts by weight of N-dimethylaniline (5 mols), and 425 parts by weight of a 37 per cent by weight aqueous formaldehyde solution (about 5 mols of anhydrous formaldehyde) along with 80 parts by weight of Filtrol clay (activated montmorillonite) as a catalyst. The mixture was refluxed and agitated at 210° F. for a period of 5 hours, and then all water, both that added with the formaldehyde and formed with the reaction, was distilled off. Thereafter, 805 parts by weight of a mineral oil having a viscosity of 72 S. U. S. at 100° F. were added, and the mixture was filtered through Celite (a diatomaceous earth). The diluted product was then neutralized with 9 parts by weight of cyclohexylamine and had the following properties:

Specific Gravity, 60°/60° F	0.9548
Color, NPA	5.5
Neutralization No	nil

Example II.—Into a reaction vessel were charged 1 mol of phenothiazine, 9 mols of N-dimethylaniline, 9 mols of formaldehyde and 10 per cent by weight of Filtrol as a catalyst. The mixture was refluxed and agitated at 210° F. for 6 hours, and then the temperature was raised to 280° F. and all water, both that added with the formaldehyde and formed with the reaction, was distilled off. The product was then filtered and neutralized with 0.2 mol of cyclohexylamine. The neutralized product had the following properties:

Specific Gravity, 60°/60° F	0.9520
Color, NPA	5.0
Neutralization No	nil

Example III.—Another product was prepared

by reacting 1 mol of phenothiazine, 4 mols of N-dimethylaniline and 4 mols of formaldehyde in the presence of 5 per cent by weight of the total reactants of an activated clay catalyst under the conditions set forth in Example I. The product was filtered, neutralized with 0.06 mol of cyclohexylamine and had the following properties:

Specific Gravity, 60°/60° F	0.9556
Color, NPA	6.0
Neutralization No	nil

The neutralized condensation products obtained in accordance with the above disclosure from phenothiazine, N-dimethylaniline and formaldehyde condensed in the presence of an activated clay catalyst and neutralized with cyclohexylamine are excellent addition agents for mineral oil lubricants. They are readily soluble in all types of mineral oils, that is, paraffinic, naphthenic or mixed base mineral oils in high proportions to form concentrated solutions thereof, which may then be diluted down to the proportions desired in the final mineral oil lubricant composition. As stated our new addition agents are remarkably effective in inhibiting the oxidative deterioration of mineral oil lubricant compositions. For this purpose small amounts of our new addition agents are generally sufficient. For example, our addition agents may be added to mineral lubricating oils in minor amounts, say from 0.001 to 1 per cent by weight of the mineral oil, sufficient to inhibit the oxidative deterioration of the oil. Larger amounts of our new addition agents may be used if desired, but it is ordinarily unnecessary to do so.

The following examples illustrate the remarkable antioxidant effects of our new addition agents. In the following examples, the base oil and the same oil blended with our new addition agents are subjected to a standard oxidation test which measures the stability of the oils to oxidation. The oxidation test referred to is a standard test designated ASTM D943–47T. 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. The flow of oxygen is maintained at 3 liters per hour. The remarkably effective stability to oxidation of mineral oil lubricant compositions containing our new addition agents is illustrated by the results shown in the following examples.

Example IV.—To a steam turbine oil having a viscosity of 150 S. U. S. at 100° F. there was added 0.5 per cent by weight of an addition agent prepared according to Example I. The base oil and the oil blended with the antioxidant were then subjected to the above described standard oxidation test with the following results:

	Base Oil	Improved Oil Containing 0.5% Antioxidant
Gravity, °API	31.7	31.6
Oxidation Text, ASTM D943-47T. 203° F., 3 L. Oxygen/Hr.:		
Time Oxidized, Hrs	180	2,931
Neutralization No.	2.0	2.0

Example V.—To a motor oil which had been highly refined by aluminum chloride treatment there was added 0.5 per cent by weight of an antioxidant prepared according to Example II.

A comparison of the base oil and improved oil follows:

	Base Oil	Improved Oil
Gravity, °API	29.3	29.2
Viscosity, SUV at 130° F	238	237
Color, NPA	2.0	2.0
Neutralization No	0.03	0.03
Oxidation Test, ASTM D943-47T 203° F., 3 L. Oxygen/Hr.:		
Time Oxidized, Hrs	170	2,880
Neutralization No	2.0	2.0

The above examples 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.

The remarkable effects of our new addition agent cannot be readily accounted for and cannot be predicted from the nature of the reactants. Thus, products prepared from other functionally similar compounds have been found to be either pro-oxidant or to show no antioxidant effects whatsoever. For example, we have prepared a neutralized condensation product similar to our new addition agent by substituting aniline for dimethylaniline. The resulting product was found to be entirely unsuitable for inhibiting the oxidative deterioration of mineral oil lubricant compositions.

Other known addition agents may be incorporated into the lubricant compositions prepared in accordance with our invention. For example, pour point depressants, extreme-pressure agents, viscosity index improvers and the like may be added. While we have shown in the examples the preparation of compounded lubricating oils, our invention is not limited thereto but comprises all mineral oil lubricant compositions containing our new addition agents, such as greases and the like.

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. The process of preparing an addition agent for mineral oil lubricants which comprises heating phenothiazine with from 4 to 9 mols of N-dimethylaniline and 4 to 9 mols of formaldehyde per mol of phenothiazine in the presence of an activated clay catalyst at a temperature not in excess of 350° F. to condense together the three reactants, recovering the condensation product and neutralizing it with cyclohexylamine.

2. The process of preparing an addition agent for mineral oil lubricants which comprises heating phenothiazine with from 4 to 9 mols of N-dimethylaniline and 4 to 9 mols of formaldehyde per mol of phenothiazine in the presence of 5 to 10 per cent by weight of the total reactants of an activated clay catalyst at a temperature of from 150° to 300° F. to condense together the three reactants, recovering the condensation product and neutralizing it with cyclohexylamine.

3. The process of preparing an addition agent for mineral oil lubricants which comprises heating a mixture consisting of an activated clay catalyst, phenothiazine with from 4 to 9 mols of N-dimethylaniline and 4 to 9 mols of formaldehyde per mol of phenothiazine to a temperature not in excess of 350° F. to form a condensation product, diluting the condensation product with a mineral lubricating oil, filtering off the catalyst, and neutralizing the filtrate with cyclohexylamine.

4. The process of preparing an addition agent for mineral oil lubricants which comprises heating 1 mol of phenothiazine, 5 mols of N-dimethylaniline, and 5 mols of formaldehyde in the presence of an activated clay catalyst at a temperature of from 150° to 300° F. to condense together the three reactants, recovering the condensation product and neutralizing it with cyclohexylamine.

5. The process of preparing an addition agent for mineral oil lubricants which comprises heating 1 mol of phenothiazine, 9 mols of N-dimethylaniline and 9 mols of formaldehyde in the presence of an activated clay catalyst at a temperature of from 150° to 300° F. to condense together the three reactants, recovering the condensation product and neutralizing it with cyclohexylamine.

6. The process of preparing an addition agent for mineral oil lubricants which comprises heating 1 mol of phenothiazine, 4 mols of N-dimethylaniline and 4 mols of formaldehyde in the presence of an activated clay catalyst at a temperature of from 150° to 300° F. to condense together the three reactants, recovering the condensation product and neutralizing it with cyclohexylamine.

7. A non-resinous condensation product of phenothiazine with from 4 to 9 mols of N-dimethylaniline and 4 to 9 mols of formaldehyde per mol of phenothiazine, said product having been neutralized with cyclohexylamine and being obtained by the process of claim 1.

8. A non-resinous condensation product of 1 mol of phenothiazine, 5 mols of N-dimethylaniline and 5 mols of formaldehyde, said product having been neutralized with cyclohexylamine and being obtained by the process of claim 4.

9. A non-resinous condensation product of 1 mol of phenothiazine with 9 mols of N-dimethylaniline and 9 mols of formaldehyde, said product having been neutralized with cyclohexylamine and being obtained by the process of claim 5.

10. A non-resinous condensation product of 1 mol of phenothiazine with 4 mols of N-dimethylaniline and 4 mols of formaldehyde, said product having been neutralized with cyclohexylamine and being obtained by the process of claim 6.

11. A lubricant composition comprising a major amount of a mineral lubricating oil, and a minor amount, sufficient to inhibit the oxidative deterioration of said oil of a non-resinous condensation product of phenothiazine with from 4 to 9 mols of N-dimethylaniline and 4 to 9 mols of formaldehyde per mol of phenothiazine, said product having been neutralized with cyclohexylamine and being obtained by the process of claim 1.

12. A lubricant composition comprising a major amount of a mineral lubricating oil, and a minor amount, from 0.0001 to 1.0 per cent by weight of said oil, of a non-resinous condensation product of phenothiazine with from 4 to 9 mols of N-dimethylaniline and 4 to 9 mols of formaldehyde per mol of phenothiazine, said product having been neutralized with cyclohexylamine and being obtained by the process of claim 1.

13. A lubricant composition comprising a major amount of a mineral lubricating oil, and a minor amount, sufficient to inhibit the oxidative

deterioration of said oil of a non-resinous condensation product of 1 mol of phenothiazine, 5 mols of N-dimethylaniline and 5 mols of formaldehyde, said product having been neutralized with cyclohexylamine and being obtained by the process of claim 4.

14. The composition of claim 13, wherein said neutralized condensation product is present in an amount of 0.5 per cent by weight.

15. A lubricant composition comprising a major amount of a mineral lubricating oil, and a minor amount, sufficient to inhibit the oxidative deterioration of said oil of a non-resinous condensation product of 1 mol of phenothiazine, 9 mols of N-dimethylaniline and 9 mols of formaldehyde, said product having been neutralized with cyclohexylamine and being obtained by the process of claim 5.

16. A lubricant composition comprising a major amount of a mineral lubricating oil, and a minor amount, sufficient to inhibit the oxidative deterioration of said oil of a non-resinous condensation product of 1 mol of phenothiazine, 4 mols of N-dimethylaniline and 4 mols of formaldehyde, said product having been neutralized with cyclohexylamine and being obtained by the process of claim 6.

17. The composition of claim 15, wherein said neutralized condensation product is present in an amount of 0.5 per cent by weight.

18. The composition of claim 16, wherein said neutralized condensation product is present in an amount of 0.5 per cent by weight.

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