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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 effects 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 has heretofore been proposed to employ as oxidation inhibitors diamino diaryl alkanes, such as tetramethyl- and tetraethyldiamino diphenyl methane. However, the antioxidant potency of such compounds has not been entirely satisfactory because it is relatively low.

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 a further object of this invention to provide improved 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 an N-diethyltoluidine and formaldehyde in the presence of an activated clay catalyst, and recovering the condensation product. The condensation product so obtained is a light-colored product which, when added to mineral oil lubricants, confers a remarkable stability against deterioration by oxidation. Such condensation products and the 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 in accordance with our invention, there are obtained light-colored condensation products which are non-resinous and which are readily soluble in mineral oils.

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Any of the isomeric N-diethyltoluidines, that is, the ortho, meta and para N-diethyltoluidines, or mixtures thereof, may be employed in accordance with our invention.

In performing the condensation, the reactants 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 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 vary as follows. For each mol of the N-diethyltoluidine, there is employed from 0.5 to 1 mol of formaldehyde. 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.

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 may be employed in accordance with our invention. 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 1,898,165, for example.

In preparing our new addition agents, the reactants and catalyst are placed into 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. In some instances, it is desirable to prepare our new addi-

tion agent in 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 the condensation product obtained will then be a concentrated solution of the addition agent in the mineral lubricating oil.

The condensation products obtained in accordance with out invention are liquids or crystalline solids. While the exact nature of the chemical composition of the condensation products is unknown, the reactants enter into a unitary product. The exact 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 may be obtained.

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

Example I.—Into an iron reaction vessel, equipped with means for agitation and a reflux condenser, there were placed 2 mols of N-diethyl-m-toluidine, 1 mol of formaldehyde in a 37 per cent by weight aqueous solution, and 10 per cent by weight of the reactants of Filtrol (an activated montmorillonite) as a catalyst. The mixture was agitated and refluxed at 210° F. for 10 hours, and then all water, both that added with the formaldehyde and formed in the reaction, was distilled off by heating at 280° F. and the product dried. The product was then filtered through Celite, a diatomaceous earth filter aid. The product had the following properties:

Gravity, °A. P. I.	11.4
Color, N. P. A.	3.75
Neutralization No.	0.36

Example II.—An addition agent was prepared by reacting 6 mols of N-diethyl-m-toluidine and 5 mols of formaldehyde in the presence of 10 per cent by weight of the total reactants of an activated montmorillonite catalyst (Filtrol) under the conditions set forth in Example I. The product had the following properties:

Gravit, °A. P. I.	10.8
Color, N. P. A.	4.0
Neutralization No.	0.45

Example III.—An addition agent was prepared by reacting 3 mols of N-diethyl-m-toluidine and 2 mols of formaldehyde in the presence of 5 per cent by weight of the total reactants of an activated clay (montmorillonite) catalyst under the the conditions set forth in Example I. The product had the following properties:

Gravity, °A. P. I.	9.9
Color, N. P. A.	5.0
Neutralization No.	1.2

The condensation products obtained in accordance with the above disclosure from an N-diethyltoluidine and formaldehyde in the presence of an activated clay catalyst 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 and can be blended with 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 on 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 A. S. T. M. 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.—An improved steam turbine oil was prepared by adding 0.5 per cent by weight of the addition agent prepared in accordance with Example I to a turbine oil base. A comparison of the base oil and the base oil blended with the antioxidant showed the following results:

	Base Oil	Improved Oil
Gravity, ° API	28.6	28.5
Oxidation Test ASTM D943-47T 203° F., 3 L. Oxygen per Hr.		
Time Oxidized, Hrs.	180	3,350
Neutralization No.	2.0	2.0

Example V.—To a refined motor oil base, there was added 0.5 per cent by weight of the addition agent prepared in accordance with Example III. A comparison of the base oil and improved oil follows:

	Base Oil	Improved Oil
Gravity, ° API	27.8	27.7
Viscosity, SUV: 130° F.	248	246
Color, NPA	3.0	3.0
Neutralization No.	0.01	0.02
Oxidation Test, ASTM D943-47T 203° F., 3 L. Oxygen per Hr.:		
Time Oxidized, Hrs.	195	3,505
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 agents cannot be readily accounted for and cannot be predicted from the nature of the react-

ants. Thus, condensation products prepared from other functionally similar compounds have been found to be either prooxidant or to show no antioxidant effects whatsoever. For example, we have prepared condensation products similar to our new addition agent by substituting aryl amines such as toluidine, xylidine, or N-diethylaniline for the N-diethyltoluidine. The resulting condensation products were found to be entirely unsuitable for inhibiting the oxidative deterioration of mineral oil lubricant compositions.

As has been shown in our copending application Serial No. 66,585, filed of even date herewith, which describes and claims the condensation of N-dimethylaniline and formaldehyde to produce excellent antioxidants for mineral lubricating oils, the type of amine used to condense with the formaldehyde is highly critical and can only be determined by experiment. This is particularly apparent in the instant application when it is considered that a condensation product of N-diethylaniline and formaldehyde (prepared exactly as the condensation product of N-diethyltoluidine and formaldehyde of this invention) fails to improve the oxidation stability of a mineral lubricating oil when added thereto in an amount of 0.5 per cent; whereas, the use of N-diethyltoluidine, a homologue of N-diethylaniline, yields excellent antioxidants. We have also found that mixtures of N-diethyltoluidine and N-dimethylaniline may be condensed with formaldehyde to produce excellent antioxidants. This is described and claimed in our copending application Serial No. 66,587, filed of even date herewith. Although N-diethylaniline when condensed alone with formaldehyde does not yield a satisfactory antioxidant, when mixtures of N-diethylaniline and N-dimethylaniline are condensed with formaldehyde in the presence of an activated clay, good antioxidants are obtained. This is described and claimed in our copending application Serial No. 66,588, filed of even date herewith.

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. If desired, 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.

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 1 mol of an N-diethyltoluidine with from 0.5 to 1 mol of formaldehyde in the presence of an activated clay catalyst at a temperature not in excess of 350° F. to condense together the reactants, and recovering the condensation product.

2. The process of preparing an addition agent for mineral oil lubricants which comprises heating 1 mol of an N-diethyltoluidine with from 0.5 to 1 mol of formaldehyde in the presence of 5 to 10 per cent by weight on the total reactants of an activated clay catalyst at a temperature of from 150° to 300° F. to condense together the reactants, and recovering the condensation product.

3. The process of preparing an addition agent for mineral oil lubricants which comprises adding an activated clay catalyst, 1 mol of an N-diethyltoluidine and from 0.5 to 1 mol of formaldehyde to a mineral lubricating oil, heating the mixture to a temperature not in excess of 350° F. to form a condensation product, and recovering a solution of the condensation product in the mineral lubricating oil.

4. The process of preparing an addition agent for mineral oil lubricants which comprises heating 2 mols of N-diethyl-m-toluidine and 1 mol of formaldehyde in the presence of about 5 to 10 per cent by weight on the total reactants of an activated clay catalyst at a temperature of from 150° to 300° F. to condense together the reactants, and recovering the condensation product.

5. The process of preparing an addition agent for mineral oil lubricants which comprises heating 6 mols of N-diethyl-m-toluidine and 5 mols of formaldehyde in the presence of about 5 to 10 per cent by weight on the total reactants of an activated clay catalyst at a temperature of from 150° to 300° F. to condense together the reactants, and recovering the condensation product.

6. The process of preparing an addition agent for mineral oil lubricants which comprises heating 3 mols of N-diethyl-m-toluidine and 2 mols of formaldehyde in the presence of about 5 to 10 per cent by weight on the total reactants of an activated clay catalyst at a temperature of from 150° to 300° F. to condense together the reactants, and recovering the condensation product.

7. A non-resinous condensation product of 1 mol of an N-diethyltoluidine with from 0.5 to 1 mol of formaldehyde, said product being obtained by the process of claim 1.

8. A non-resinous condensation product of 2 mols of N-diethyl-m-toluidine and 1 mol of formaldehyde, said product being obtained by the process of claim 4.

9. A non-resinous condensation product of 6 mols of N-diethyl-m-toluidine and 5 mols of formaldehyde, said product being obtained by the process of claim 5.

10. A non-resinous condensation product of 3 mols of N-diethyl-m-toluidine and 2 mols of formaldehyde, said product 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 one mol of an N-diethyltoluidine with from 0.5 to 1 mol of formaldehyde, said product 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 0.001 to 1.0 per cent by weight of said oil, of a non-resinous condensation product of an N-diethyltoluidine with from 0.5 to 1 mol of formaldehyde, said product 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 2 mols of N-diethyl-m-toluidine and 1 mol of formaldehyde, said product being obtained by the process of claim 4.

14. 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 6 mols of N-diethyl-m-toluidine

and 5 mols of formaldehyde, said product being obtained by the process of claim 5.

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 3 mols of N-diethyl-m-toluidine and 2 mols of formaldehyde, said product being obtained by the process of claim 6.

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

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

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

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