Patented Feb. 14, 1950

2,497,099

UNITED STATES PATENT OFFICE

2,497,099

ADDITION AGENTS FOR MINERAL OIL LUBRICANTS AND COMPOSITIONS CONTAINING THE SAME

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No Drawing. Application June 12, 1947, Serial No. 754,268

21 Claims. (Cl. 252—42.7)

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This invention relates to addition agents for mineral oil lubricants and compositions containing the same, and more particularly, it is concerned with addition agents for mineral oil lubricants which provide detergent effects and inhibit the oxidative deterioration of said lubricants.

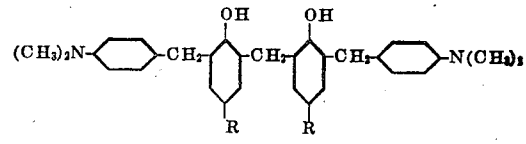
In the lubrication of internal combustion engines of all types, particularly when severe operating conditions are encountered, plain mineral lubricating oils often prove unsatisfactory in service because of the oxidative deterioration of the oil with the attendant deposition on the engine surfaces of varnish, gum and sludge. In turbine oils, the problem of oxidation is further aggravated because in normal use turbine oils rapidly become contaminated with water.

The formation of varnishes, gums and sludges on engine surfaces is due, at least in part, to oxidation effects on the mineral lubricating oils. The presence of these substances is disadvantageous because the oxidation products of the oil tend to increase ring sticking and the production of further deposits on piston surfaces and in fixed parts of the combustion chamber. Sludges are formed in the crank case of the engine and the rate of corrosion of bearing surfaces is increased, especially with bearing alloys of the types now in use.

It is an object of this invention, therefore, to provide an addition agent for mineral oil lubricants which will prevent the formation of the engine deposits encountered in the use of mineral oil lubricants. It is a further object of this invention to provide an addition agent for mineral oil lubricants which will inhibit the oxidative deterioration of such lubricants. It is a still further object of this invention to provide an addition agent for mineral oil lubricants which serves the functions of (1) inhibiting the oxidative deterioration of the lubricant and (2) acting as a detergent to prevent ring sticking, varnishing or coating of the metallic surfaces of internal combustion engines, as well as a suspending or dispersing agent for dispersing very small particles of deterioration products or contaminating materials in the oil.

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These and other objects are achieved by the present invention wherein there is provided as an addition agent for mineral oil lubricants a substantially neutral polyvalent metal salt of a compound having the formula:



wherein R is an alkyl radical having from 4 to 12 carbon atoms. We have found that the above described polyvalent metal salts have excellent solubility in mineral oils and will effectively act as detergents. Most of the salts will also act to inhibit the oxidative deterioration of said lubricants.

The substantially neutral polyvalent metal salts of our invention are prepared by the condensation of N-dimethylaniline, a phenol having a para-alkyl substituent of from 4 to 12 carbon atoms and formaldehyde. More specifically 2 mols of the alkylated phenol, 2 mols of N-dimethylaniline and 3 mols of formaldehyde are condensed in the presence of an activated clay catalyst, such as bentonite, fuller's earth, floridin and the like which has been acid treated in order to activate the clay. The condensation is performed by heating the reactants to a maximum temperature of 350° F., preferably at a temperature ranging from 150° to 300° F. The condensation may be considered complete when all of the formaldehyde is consumed, and results in the splitting off of 3 mols of water. The activated clay catalyst is preferably used in an amount of 5 to 10 per cent by weight of the total reactants, and serves the function of promoting the formation of light-colored, oil-soluble condensation products which are non-resinous in nature, instead of resinous, highly-condensed insoluble materials. In lieu of formaldehyde, any formaldehyde-yielding compound, such as para-formaldehyde, trioxymethylene and the like, may be em-

ployed. In such case, the amount of formaldehyde-yielding compound used is based on the equivalent number of mols of formaldehyde yielded. Accordingly, as used herein, the term "formaldehyde" is intended to include formaldehyde-yielding compounds, as well as formaldehyde itself.

The product resulting from the above described condensation is then reacted with a polyvalent metal hydroxide or oxide in an amount sufficient to result in a substantially neutral salt. Alternatively, the salts may be prepared in one step by mixing the polyvalent metal hydroxide or oxide, N-dimethylaniline, the phenol and formaldehyde together and reacting the mixture. In lieu of forming the metal salts by reaction with the polyvalent metal oxide or hydroxide, alkali metal salts may first be formed by neutralization of the condensation product with an alkali metal hydroxide followed by a double decomposition reaction of the alkali metal salt with a water-soluble salt of a desired polyvalent metal.

The para alkyl phenol used in preparing our new addition agents has from 4 to 12 carbon atoms in the alkyl group, and may thus include para alkyl phenols such as butyl, amyl, hexyl, heptyl, octyl, decyl and dodecyl phenols. The alkyl group may have a normal or branched chain structure. Such alkyl phenols are conveniently prepared by alkylating, in the presence of a condensing agent such as concentrated sulfuric acid, phenol with an olefin, such as butene-1, isobutylene, the various amylenes, di-isobutylene and tri-isobutylene. A preferred phenol is para-tetramethylbutyl phenol obtained by alkylating phenol with di-isobutylene in the presence of concentrated sulfuric acid.

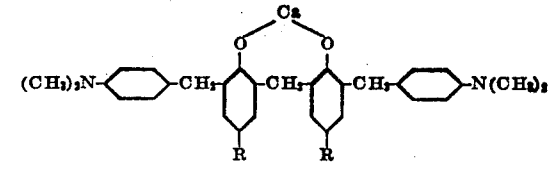
As has been stated, the addition agents of our invention are polyvalent metal salts. Polyvalent metals which may be used include divalent metals such as beryllium, barium, calcium, strontium, magnesium, zinc, cadmium, copper, lead, nickel, cobalt, etc. Trivalent metals such as aluminum, bismuth and chromium, as well as metals of higher valency, such as tin, may also be employed. A preferred subgroup of polyvalent metals comprises the alkaline earth metals. Whereas all polyvalent metals form excellent oil-soluble detergent salts in accordance with our invention, not all of them will yield salts which inhibit the oxidative deterioration of mineral oil lubricants. Thus the copper and lead salts will not ordinarily inhibit oxidative deterioration. However, where in addition to detergency, antioxidant properties must be conferred on a mineral oil lubricant, either the antioxidant salts of our invention or other known antioxidant compounds may be added in an amount sufficient to confer the desired effect.

The following example illustrates the preparation of our new addition agents:

Example I.—Para-tetramethylbutyl phenol was conveniently prepared by introducing 24.8 parts by weight of phenol and 31.4 parts by weight of commercial di-isobutylene polymer into a reaction vessel. The mixture was then agitated and 1.2 parts by weight of 94–98% sulfuric acid were added over a period of 30 minutes. After the addition of the sulfuric acid, the temperature was maintained at 220° F. for a period of 24 hours. The reaction mixture was then cooled to 180° F. and was washed three times with 10 parts by weight of water. The reaction temperature was not permitted to exceed 220° F. Four hundred twelve pounds of the resulting para-tetramethylbutyl phenol were placed in a reaction vessel along with 242 pounds of N-dimethylaniline, 245 pounds of 37% aqueous formaldehyde, 74 pounds of hydrated lime and 10 per cent by weight of the total reactants of an acid activated bentonite clay. The vessel was then closed, attached to a reflux condenser and refluxed 6 hours at 210° F. The water was then stripped off, the temperature raised to 295° F. and the product filtered. The product had the following properties:

Gravity, °API	6.7
Color, NPA	5.5
Neutralization No	1.68
Ash: per cent	7.7

The product obtained was the substantially neutral calcium salt of bis (2-hydroxy, 3-paradimethylaminobenzyl, 5-tetramethylbutyl, phenyl) methane having the formula:



wherein R is the tetramethylbutyl radical. This product was a highly viscous liquid.

The barium and aluminum salts of bis (2-hydroxy, 3-paradimethylaminobenzyl, 5-tetramethylbutyl, phenyl) methane were prepared by a procedure identical with that shown in Example I, except that an amount of mineral lubricating oil equal to the weight of the reactants was added. The resulting solutions of the barium and aluminum salts had the following properties:

	Barium salt in oil solution	Aluminum salt in oil solution
Gravity, °API	12.5	12.7
Color, NPA	4.25	4.5
Neutralization No	(1)	0.8
Ash, percent	9.0	3.5

[1] Slightly alkaline.

The metal salts disclosed hereinabove are excellent addition agents for mineral oil lubricant compositions. They are readily soluble in all types of mineral oils, that is, paraffinic, naphthenic, or mixed base mineral oils and can be blended with them in high proportions. This excellent solubility of our new addition agents enables the preparation of 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 confer excellent detergent properties on the mineral lubricating oils with which they are incorporated, and in most instances also inhibit oxidative deterioration of the mineral lubricating oil. For these purposes our new addition agents are generally added in minor amounts, say from 0.1 to 10.0 per cent by weight on the mineral oil. Ordinarily, 0.1 per cent by weight is sufficient to effect the desired improvement.

The following examples illustrate the remarkable improvements effected by the use of our new addition agents.

Example II.—An improved motor oil was prepared by treating a motor oil which had been highly refined with aluminum chloride with 0.5% by weight of the addition agent prepared in ac-

cordance with Example I. A comparison of the improved oil and base oil follows:

	Base Oil	Improved Oil
Gravity, ° API	29.5	29.4
Viscosity, SUV, 130° F.	235	231
Color, NPA	2.0	2.0
Neutralization No.	0.01	0.02
Oxidation Test:		
ASTM-Proposed—		
203° F., 3 L. Oxygen/Hr.:		
Time Oxidized, Hr.	210	2000+
Neutralization No.	2.0	
Motor Oil Service Test:		
Method 259, Gulf—		
Piston Condition No.	4	1

Example III.—An improved steam turbine oil was prepared by treating a base turbine oil stock with 0.5% by weight of the agent prepared according to Example I. A comparison of the improved oil and base oil follows:

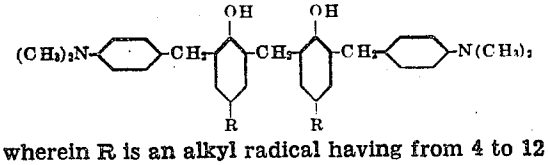
	Base Oil	Improved Oil
Gravity, ° API	26.8	26.6
Oxidation Test:		
ASTM-Proposed—		
203° F., 3 L. Oxygen/Hr.:		
Time Oxidized, Hr.	180	2000+
Neutralization No.	2.0	

The above examples show the remarkable oxidation stability imparted to mineral oil lubricants by the use of our new addition agents, as well as the effective detergent effects obtained. The oxidation test referred to is a standard test described in "ASTM Standards on Petroleum Products and Lubricants," September 1943, pages 17–20. 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. As may be seen from the above examples, an oxidation stability of more than 2000 hours had already been attained but the neutralization number had not yet reached 2. The motor oil service test referred to in Example II is fully described in U. S. Patent 2,378,442.

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.

We claim:

1. A substantially neutral polyvalent metal salt of a compound having the formula:



wherein R is an alkyl radical having from 4 to 12 carbon atoms.

2. The salt of claim 1, wherein the metal salt is a divalent metal salt.

3. The salt of claim 1, wherein the metal salt is a trivalent metal salt.

4. The salt of claim 1, wherein the metal salt is an alkaline earth metal salt.

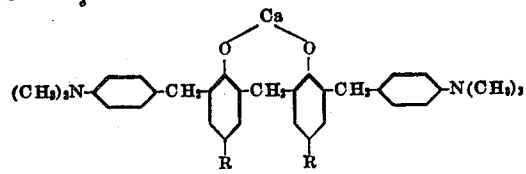
5. The salt of claim 1, wherein the metal salt is a calcium salt.

6. The salt of claim 1, wherein the metal salt is a barium salt.

7. The salt of claim 1, wherein the metal salt is an aluminum salt.

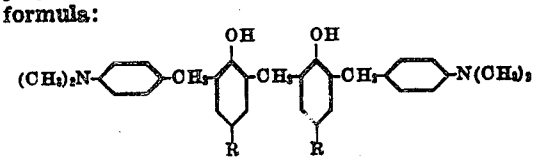
8. The salt of claim 1, wherein R is the tetramethylbutyl radical.

9. The substantially neutral calcium salt of bis (2-hydroxy, 3-paradimethylaminobenzyl, 5-tetramethylbutyl, phenyl) methane, having the formula:



wherein R is the tetramethylbutyl radical.

10. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to confer detergent properties on the composition, of a substantially neutral polyvalent metal salt of a compound having the formula:



wherein R is an alkyl radical having from 4 to 12 carbon atoms.

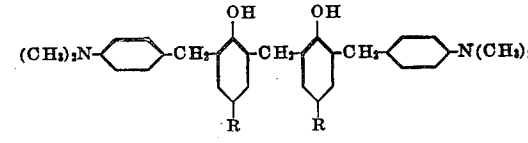
11. The composition of claim 10, wherein the metal salt is a divalent metal salt.

12. The composition of claim 10, wherein the metal salt is a trivalent metal salt.

13. The composition of claim 10, wherein the metal salt is an alkaline earth metal salt.

14. The composition of claim 10, wherein the metal salt is present in an amount of from 0.1 to 10.0 per cent by weight on the mineral oil.

15. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, from 0.1 to 10.0 per cent by weight on the mineral lubricating oil, of a substantially neutral polyvalent metal salt of a compound having the formula:



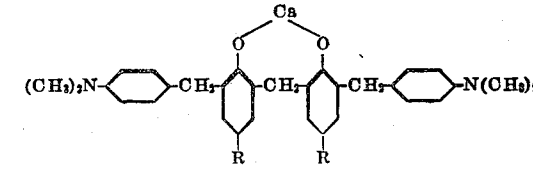
wherein R is the tetramethylbutyl radical.

16. The composition of claim 15, wherein the metal salt is a calcium salt.

17. The composition of claim 15, wherein the metal salt is a barium salt.

18. The composition of claim 15, wherein the metal salt is an aluminum salt.

19. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to confer detergent and antioxidant properties on the composition, of the substantially neutral calcium salt of bis (2-hydroxy, 3-paradimethylaminobenzyl, 5-tetramethylbutyl, phenyl) methane having the formula:



wherein R is the tetramethylbutyl radical.

20. The process which comprises forming a substantially neutral polyvalent metal salt of a compound obtained by condensing 2 mols of

a phenol having a para-alkyl substituent of from 4 to 12 carbon atoms, 2 mols of N-dimethylaniline and 3 mols of formaldehyde in the presence of an activated clay catalyst.

21. The process which comprises forming in a mineral lubricating oil a substantially neutral polyvalent metal salt obtained by condensing at a temperature not in excess of 350° F. 2 mols of a phenol having a para-alkyl substituent of from 4 to 12 carbon atoms, 2 mols of N-dimethylaniline and 3 mols of formaldehyde in the presence of an activated clay catalyst, and recovering a solution in said mineral lubricating oil of the substantially neutral polyvalent metal salt so obtained.

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TROY L. CANTRELL.
JOHN G. PETERS.

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