United States Patent Office 3,018,248
Patented Jan. 23, 1962

3,018,248

OXIDATION INHIBITED MINERAL OIL COMPOSITIONS

Edward G. Foehr, San Rafael, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

No Drawing. Filed Jan. 20, 1960, Ser. No. 3,481
8 Claims. (Cl. 252—37)

This invention relates to the stabilization of organic liquids from the deleterious effects of oxidation, particularly to the stabilization of lubricating oil compositions intended for use in the service of transformer oils, turbine oils, and the like. More particularly, this invention pertains to mineral oil compositions useful as transformer oils, wherein the anti-oxidation characteristics of certain anti-oxidants present in the composition have been enhanced by the presence of certain metal salts of organic acids.

The effectiveness of transformer oils as insulating oils is materially reduced by the oxidation products (i.e., the acid products) formed. Furthermore, these acid products gradually attack the insulation on the wires of the transformer system, leaving the wires partially exposed to the oil, which oil then serves as a transmitter of current instead of an inhibitor of current. In the turbine oils the oxidation products (i.e., the acid sludges) corrode the bearings and other parts of the turbine system and clog the oil lines, etc.

It is a tremendous advantage in transformer, turbine, and like systems, to use the oils of sufficient oxidation stability to permit their use over long periods of time without being changed. Not only is it desirable to have transformer oils and the like highly resistant to oxidation, but it is also a desired feature of the transformer oils and the like that the viscosity index be high; that is, that only small changes in viscosity occur with large changes in temperature. Thus, in order to obtain oils of high viscosity index, the base oils are subjected to such effective methods of refining as the selective solvent extraction processes wherein the lower viscosity index hydrocarbons are selectively dissolved. These selective solvent refining processes concentrate in one fraction, usually the undissolved oil fraction, those compounds of a "paraffinic" nature which show a smaller change in viscosity upon change in temperature. However, highly refined oils have smaller amounts of the naturally occurring oxidation inhibitors present in the oils than do less refined oils. That is, these naturally occurring inhibitors have been removed at least to an extent which materially reduces the oxidation stability of the oil when used as transformer oils and as turbine oils.

When oxidation inhibitors are added to highly refined oils and oils which are not so highly refined, it is found that the highly refined oils are more responsive to the oxidation inhibitors; that is, when the oxidation inhibitors of this invention are incorporated in so-called over-refined oils, a greater resistance to oxidation is obtained than when the oxidation inhibitors are used in conjunction with a less refined lubricating oil.

In attempting to increase the oxidation stability of transformer and turbine oils, known oxidation inhibitors (e.g., 2,6-di-tertiary-butyl-phenol) were incorporated therein, and, as expected, the resulting compounded oils were more resistant to oxidation than the base oils containing no inhibitors. However, it was not to be expected that the oxidation stability of the oil thus compounded with oxidation inhibitors could be increased still further by adding thereto certain metal salts which of themselves are known to catalyze oxidation of mineral oils.

It is known that numerous metals catalyze the formation of oxidation products in lubricating oil compositions. For example, metals such as copper and cobalt are notorious as catalysts for the oxidation of organic compounds. When large amounts of these metals are employed in lubricating oil compositions, the oxidation of the oils is accelerated, resulting in increased formation of sludges.

Although large amounts of copper compounds (e.g., copper naphthenate) have been incorporated in oil compositions, it has been necessary to use other compounds therewith to inhibit the corrosivity caused by such copper compounds. For example, when lubricating oils containing amounts in excess of 50 p.p.m. of copper are incorporated in lubricating oil compositions, it has been necessary to incorporate therewith for the purpose of imparting oil stabilizing properties to the copper, oil-soluble organic sulfur compounds. Furthermore, when using lubricating oils containing amounts of at least 0.1% of cobalt salts of organic acids (e.g., cobalt naphthenate), it has been necessary to incorporate therewith corrosion inhibitors such as esters containing amino substituents; for example, octyl alpha amino-propionate.

It is an outstanding feature of this invention that the oxidation stability of mineral oils compounded with known oxidation inhibitors is materially increased by adding thereto an agent not known as an oxidation inhibitor which agent asserts synergistic effects in combination with the oxidation inhibitors of this invention.

It is the primary object of this invention to incorporate in mineral oils containing known oxidation inhibitors small amounts of metal compounds which normally catalyze the oxidation of lubricating oil compositions.

Therefore, in accordance with this invention, oxidation-inhibited mineral oil compositions are obtained by incorporating in mineral oils containing certain phenols small amounts of certain oil-soluble metal salts. Thus, the particular oil compositions of this invention consist essentially of mineral oils, certain phenols, and in combination therewith, certain oil-soluble copper and cobalt salts of organic acids.

Contrary to the performance which might be expected therefrom, trace amounts of the particular metals cobalt and copper synergistically enhance the activity of certain phenols as oxidation inhibitors in lubricating oil compositions.

The phenols whose oxidation inhibitory effects are synergistically enhanced by the presence of small amounts of certain metal salts are tertiary butyl phenols. The tertiary butyl phenols are exemplified by 2,6-di-t-butyl-p-cresol; 2,6-di-t-butyl phenol; 2,6-di-t-butyl-α-dimethyl-amino-p-cresol; 4,4'-methylene bis(2,6-di-t-butyl phenol); 4,4'-methylene bis(6-t-butyl-o-cresol); 4,4'-bis(2,6-di-t-butyl phenol); 4,4'-thiobis(6-t-butyl-o-cresol); 2,6-di-t-butyl-α-methoxy-p-cresol, etc.

The particular metals which are effective herein to enhance the activity of the phenols as oxidation inhibitors in lubricating oil compositions are copper and cobalt. Oil-soluble organic compounds which can be used to impart copper and cobalt metals to the lubricating oil compositions include the copper and cobalt salts of organic acids such as naphthenic acids; fatty acids containing from 10 to 22 carbon atoms, for example, lauric acid, 12-hydroxy stearic acid, etc.; acids obtained by the oxidation of petroleum waxes, acids obtained from the higher boiling fractions of the refining of petroleum products, etc.

The phenol oxidation inhibitors are used in amount sufficient to inhibit oxidation of mineral oils; that is, in amounts of 0.02% to 10%, by weight, preferably 0.1% to 1%, by weight.

The organic acid salts of copper and cobalt are used

herein in amounts such that the metals copper and cobalt enhance the anti-oxidation properties of the tertiary butyl phenols; that is, in amounts sufficient to impart from 1 to 25 p.p.m. of copper metal in the lubricating oil compositions or from 1 to 200 p.p.m. of cobalt metal in the lubricating oil compositions.

The oils useful in the composition of this invention include a wide variety of lubricating oils, such as naphthenic base, paraffin base, and mixed base mineral oils, other hydrocarbon lubricants, e.g., lubricating oil derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propene, butene, etc. and mixtures thereof), alkylene oxide-type polymers (e.g., propene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing alkylene oxides, e.g., propene oxide, in the presence of water or alcohol, e.g., ethyl alcohol, and esters of alkylene oxide-type polymers, e.g., acetylated propene oxide polymers prepared by acetylating propene oxide polymers containing hydroxyl groups.

Other synthetic oils include dicarboxylic acid esters (e.g., dibutyl adipate, dihexyl adipate, di-2-ethylhexyl sebacate, condensation products of hexamethylene glycol and adipic acid, etc.); liquid esters of acids of phosphorus (e.g., tricresyl phosphate, diethyl ester of decane phosphonic acid, etc.); liquid esters of silicon and polysiloxanes (e.g., tetra(2-ethyl-hexyl) silicate, poly(methyl phenyl) siloxane, poly(methyl) siloxane, etc.

Table I hereinbelow presents data showing the marked synergism which small amounts of copper and cobalt exhibit in increasing the effectiveness of phenols as oxidation inhibitors.

The oxidation stability of the lubricating oil composition was tested by mixing oxygen with the test oil at 340° F. at atmospheric pressure for a period of time until 1 liter of oxygen had been absorbed by the lubricating oil composition. The inhibition period (IP) is the number of hours for the oil being tested to absorb 1 liter of oxygen per 100 grams of oil at 340° F.

The Base Oil was a white oil having a viscosity of 340 SUS at 100° F. The inhibition period for the Base Oil A was about 0.1 hour.

TABLE I

Inhibition period (hours)

Metal [1]	Base Oil +0.4% 2,6-Di-t-butyl-p-cresol	Base Oil +0.4% 2,6-Di-t-butyl phenol
None	10.2	5.1
Copper, p.p.m.:		
2	13.7	7.9
5	14.2	8.7; 9.3
10	13.8	10.3; 9.5
20	10.5	8.5
40	8.1	4.7
Cobalt, p.p.m.:		
1		6.2
2	13.1	14.5
5	14.0; 16.2	11.8
10	12.3	11.8
40	11.9	16.3

[1] From metal naphthenate.

The addition of 5 p.p.m. of cobalt (from cobalt naphthenate) to diethyl tetra(2-ethylhexoxy) disiloxane containing 1%, by weight, of 2,6-di-t-butyl-p-cresol increased the inhibition period from 2.1 hours to 3.0 hours. The IP of the diethyl tetra(2-ethylhexoxy) disiloxane was about 0.1 hour.

Other oxidation inhibitors whose effectiveness is enhanced by the addition to the lubricating oil compositions of copper and cobalt include phenyl alpha naphthylamine and dioctyl diphenylamine. For example, adding 5 p.p.m. of cobalt (from cobalt naphthenate) to diethyl tetra(2-ethylhexoxy) disiloxane containing 0.2%, by weight phenyl alpha naphthylamine increased the IP from 0.6 hour to 1.7 hours; and adding 5 p.p.m. and 200 p.p.m. of cobalt (from cobalt naphthenate) to diethyl tetra (2-ethylhexoxy) disiloxane containing 2%, by weight, of dioctyl diphenylamine increased the IP from 3.4 hours to 15.2 hours and 10.5 hours, respectively.

As described hereinabove, copper and cobalt metal markedly enhance the effectiveness of certain phenols as oxidation inhibitors. However, no such effects were observed with the metals iron, cerium, strontium, barium, calcium, nickel, and manganese. A slight effect was noticed with lead in amounts of 5 to 10 p.p.m.

In addition to the various additives described hereinabove, the lubricating oil compositions herein may include various thickening agents to form grease compositions, other oxidation inhibitors, corrosion inhibitors, viscosity improving agents, coloring agents, etc.

I claim:

1. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, from 0.02% to 10%, by weight, of a tertiary butyl phenol selected from the group consisting of 2,6-di-t-butyl-p-cresol and 2,6-di-t-butyl phenol, and an oil-soluble copper naphthenate in amount such that the copper is present in said lubricating oil composition in amount from 1 to 25 p.p.m.

2. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, from 0.02% to 10%, by weight, of a tertiary butyl phenol selected from the group consisting of 2,6-di-t-butyl-p-cresol and 2,6-di-t-butyl phenol, and an oil-soluble cobalt naphthenate in amount such that the cobalt is present in said lubricating oil composition in amount from 1 to 200 p.p.m.

3. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, from 0.1% to 1%, by weight, of a tertiary butyl phenol selected from the group consisting of 2,6-di-t-butyl-p-cresol and 2,6-di-t-butyl phenol, and copper naphthenate in amount such that the copper is present in said oil composition in amount from 1 to 25 p.p.m.

4. The lubricating oil composition of claim 3, wherein said phenol is 2,6-di-t-butyl phenol.

5. The lubricating oil composition of claim 3, wherein said phenol is 2,6-di-t-butyl-p-cresol.

6. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity from 0.1% to 1%, by weight, of a tertiary butyl phenol selected from the group consisting of 2,6-di-t-butyl-p-cresol and 2,6-di-t-butyl phenol, and cobalt naphthenate in amount such that the cobalt is present in said oil composition in amount from 1 to 200 p.p.m.

7. The lubricating oil composition of claim 6, wherein said phenol is 2,6-di-t-butyl phenol.

8. The lubricating oil composition of claim 6, wherein said phenol is 2,6-di-t-butyl-p-cresol.

References Cited in the file of this patent

UNITED STATES PATENTS

2,001,108	Parker	May 14, 1935
2,634,237	Kopf et al.	Apr. 7, 1953
2,671,758	Vinograd et al.	Mar. 9, 1954
2,695,273	Hook et al.	Nov. 23, 1954