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LUBRICANT COMPOSITION

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1 Claim. (Cl. 252—52)

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This invention relates to lubricants of improved quality. More particularly, an object of the invention is to provide lubricant compositions for general use which have a high degree of stability with respect to oxidation. A further important object of the invention is to provide lubricants for use in certain types of service wherein the lubricant is required to be highly resistant toward oxidation and at the same time also is required to be effective to substantially prevent rusting of the service equipment due to action of water.

It is well known that lubricating oils tend to deteriorate under service conditions, particularly through oxidation, forming undesirable substances such as acidic materials, resins, gums, sludge and the like which in one way or another result in depreciated performance. It also is known to prepare lubricant compositions having less tendency toward deterioration during service operation by utilizing in the compositions relatively small amounts of various organic substances which serve to minimize or inhibit oxidation. I have now discovered that thymol is particularly effective in stabilizing mineral oil compositions against oxidation and is well adapted to inhibiting or substantially retarding deterioration of lubricants such as petroleum lubricating oils and greases.

In accordance with the present invention lubricants of enhanced stability are prepared by incorporating thymol therein in amount sufficient to impart the desired stability characteristics. This amount may vary depending on the particular base oil employed but in any case will be relatively small. Thus, amounts ranging from a small fraction of one per cent up to three per cent, for example, may be used although, generally speaking, less than one per cent, for instance 0.1–0.5 per cent is sufficient effectively to inhibit oxidation. By adding thymol in the aforesaid proportions, a wide variety of improved petroleum oil lubricants, for example, lubricating oils for internal combustion engines, turbine oils, electrical oils, greases and the like, may be prepared.

In a special embodiment of particular utility the invention is directed to and provides lubricants which are resistant toward oxidation and which also are effective to substantially prevent rusting of the service equipment in which the lubricants are used in the presence of water. An outstanding example of a case in which the lubricant not only must have a high degree of stability toward oxidation but also must function as an anti-rust agent occurs in the operation of steam turbines. These requirements cannot necessarily

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be satisfied by the addition to the oil of a good oxidation inhibitor and a good rust-preventive. For example, various good oxidation inhibitors are water-soluble to a substantial degree and therefore, in service equipment like that above specified, are inoperative. Again, the addition of a good rust-preventive to a lubricating oil containing a good oxidation inhibitor may very substantially impair the stabilizing power of the other constituent; for example, various amines (for instance ethyl diethanolamine) are good rust-preventives but destroy the inhibiting power of oxidation inhibitors to such an extent that they are unsuitable for use in lubricants which contain the inhibitor. In accordance with the present invention both requirements are satisfactorily met by incorporating in the lubricant thymol to impart desired stability thereto and one or more compounds of a particular class of compounds which are excellent rust-preventives and which, while slightly reducing the effectiveness of the thymol as an anti-oxidant, do not impair its stabilizing power to a material degree. I have discovered that thymol functions as an effective oxidation inhibitor in the presence of water and even when used in combination with these rust-preventive compounds.

The desired rust-preventive quality of the lubricant is obtained by incorporating in the thymol-containing lubricant a relatively small amount of a substance comprising a dihydroxybenzene which has attached to the benzene ring one or more hydrocarbon groups having sufficient carbon atoms to render said substance soluble in oil and insoluble in water. I believe that any substituted dihydroxy-benzene that is water-insoluble is effective to substantially prevent rusting. The efficiency of substances of this class as a rust-preventive is due, presumably, to their capacity to cause the lubricant to wet, in the form of a thin film, the metal surfaces and thus form a protective coating that prevents effective contact between the metal and water. I have discovered that the detrimental effect of such substances upon the oxidation stability of a thymol-containing oil is so slight as to be inconsequential in comparison with their great advantage as an anti-rust agent. However it is distinctly preferred to employ, as the anti-rust agent, those compounds of the broad class of compounds specified which are derivatives of pyrocatechol (1,2-benzenediol) having a hydrocarbon group attached at the para position. This preferred class of compounds, added to lubricating oil, is disclosed in the application of W. An-

drew Wright, Serial No. 501,855 (Wright Case 1), filed of even date herewith. Such modified lubricating oil is therein broadly claimed, since it is new and useful as a rust-preventive agent as applied to equipments wherein stability of the lubricant toward oxidation is of less or little importance in comparison to that required for lubricants for use in steam turbines.

As examples of effective rust-preventing agents of the type above set forth may be mentioned the following: 4-tertiary butyl-1, 2-benzenediol; 4-tertiary octyl-1, 2-benzenediol; 4-lauryl-1, 2-benzenediol; and 4-cyclohexyl-1, 2-benzenediol. In these examples it is to be noted that the number of carbon atoms in the attached hydrocarbon groups vary from four to twelve and that in all cases the size of the hydrocarbon chains are such as to impart to the compounds the desired solubility characteristics. These compounds may be used in any effective proportion, but it is generally satisfactory to employ relatively small amounts, for example, not over 2 per cent and preferably 0.05–0.5 per cent. The stearyl derivative of pyrocatechol, which contains eighteen carbon atoms in the attached stearyl group, although having the desired solubility characteristics, is not as effective as the above named agents and therefore must be used in a greater proportion in order to afford the desired protective action. The lower effectiveness of the stearyl derivative presumably may be due to too large a number of carbon atoms in the attached hydrocarbon group; accordingly it is preferred to use derivatives having fewer carbon atoms in the attached group, for instance 4–12 carbon atoms.

The examples given below serve to illustrate the present invention but are not to be taken by way of limitation, since many modifications obviously are within the scope of the invention. In these examples the lubricants concerned are of turbine oil type and accordingly have been evaluated by a test method known as Roger's modified turbine oil stability test. In this method the lubricant in question is oxidized at 95° C. in the presence of water and metal catalysts consisting of copper and iron and under rigidly controlled conditions until the neutralization number of the oil has reached a value of 2.00 mgs. KOH per gram, the time required for reaching this value being taken arbitrarily as the life period of the sample. The longer the life period, the greater is the stability of the lubricant. This method is substantially that described in the article appearing in Industrial Engineering Chemistry, Analytical Edition, volume 13, pages 306–312 (1941), entitled "Evaluation and performance of turbine oils."

Example I

Thymol in amount equal to 0.5 per cent by weight was added to a petroleum lubricating oil having the following specifications:

Gravity	° A. P. I.	22.5
Flash point	° F.	335
Fire point	° F.	380
Saybolt Universal vis. at 100° F		155
N. P. A. color		1¾

The resulting blend was subjected to the Roger's modified turbine oil stability test, with results as given below. For comparison, the original oil was tested in like manner.

	Life period
Oil without inhibitor	hrs. 50
Blend containing 0.5% thymol	hrs. 395

From the above data it is readily apparent that thymol is an effective stabilizing agent.

Example II

A white oil having a S. U. viscosity of 150 at 100° F., prepared by treatment of a distillate fraction from a Gulf Coastal crude with 200 pounds of fuming sulfuric acid per barrel in increments of 20 pounds per barrel, was subjected to the Roger's modified turbine oil stability test. Two blends of this oil, containing 0.25 per cent and 0.50 per cent thymol respectively, also were subjected to the test, with results as follows:

	Life period
150 vis. white oil	hrs. 85
Blend containing 0.25% thymol	hrs. 1,570
Blend containing 0.50% thymol	hrs. 2,245

This tabulation clearly shows the effectiveness of thymol as an oxidation inhibitor.

Example III

The original oil of Example I was used as base stock for the preparation of a turbine oil lubricant having rust-preventive properties as well as a high degree of resistance toward oxidation. The turbine oil lubricant was prepared by blending the base stock with 0.2 per cent 4-tertiary butyl-1,2-benzenediol and 0.5 per cent thymol.

The blend was tested according to A. S. T. M. tentative method D665–42T for evaluating rust-preventing characteristics of turbine oil, described on pages 274–276 of the publication entitled, "A. S. T. M. Standards on Petroleum Products and Lubricants," issued October 1942. In this test a highly polished steel specimen is maintained in contact with oil containing 10 per cent water at a temperature of 140° F. under carefully controlled conditions for a period of 48 hours. In order that the oil pass the test the steel specimen after this period of time must be free from rust. The blend passed the test, the entire surface of the steel specimen being free from rust. Subjection of the same base stock, without the addition agents, to the same test resulted in failure, with 80 per cent of the steel specimen exhibiting rust.

The oxidation stability of the blend was determined by means of the Roger's modified turbine oil stability test and the life period of the blend was found to be 333 hours, as compared to 50 hours for the unblended stock and 395 hours for the stock blended with 0.5 per cent thymol but with no anti-rust agent (see Example I). This demonstrates that the stabilizing quality of the thymol was not seriously adversely affected by the addition of the anti-rust agent. By way of contrast, a blend of the same base stock with 0.1 per cent ethyl diethanolamine and 0.5 per cent thymol, although having satisfactory rust-preventive qualities by virtue of the presence of the ethyl diethanolamine, had a life period of only 58 hours; thus showing that this particular anti-rust agent, in contrast to the anti-rust agents of the present invention, substantially destroyed the stabilizing quality of the thymol.

In the appended claims whenever reference is made to a substituted dihydroxy-benzene, it should be understood that this refers to a compound resulting from replacement of nuclear hydrogen in a dihydroxy-benzene by at least one hydrocarbon group.

What I claim and desire to protect by Letters Patent is:

A mineral oil lubricant composition containing

a small proportion of thymol effective to substantially inhibit oxidation and a small rust-preventive proportion of a substance comprising a substituted 1,2-dihydroxy-benzene having as the substituent a saturated aliphatic hydrocarbon group attached to the benzene ring in the para position and containing 4–12 carbon atoms.

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