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TURBINE OIL

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This invention relates to improvements in turbine oils and more particularly relates to turbine oils having improved resistance to oxidation and to inhibitors for preventing rust formation of steam turbines.

It has been found that rust formation and corrosion of the working parts of steam turbines occurs when lubricated with ordinary mineral oils. We have found that the deterioration of turbine oils and rusting of the turbines can be materially inhibited by adding to mineral turbine oils a small amount of "acid oil" obtained by neutralization of spent caustic alkali solutions resulting from the treatment of straight-run and cracked light petroleum distillates such as kerosene and gasoline with caustic alkali solution to remove therefrom sulfur compounds, phenolic compounds and acids.

An object of our invention is to provide an improved turbine oil.

Another object of our invention is to provide a method for inhibiting turbine oils against oxidation while in use.

A further object of our invention is to provide an inhibitor suitable for inhibiting oxidation of mineral oils and rusting of steam turbines.

Further objects of the invention will appear from the following description.

In accordance with our invention used caustic alkali solution, which is partially or substantially completely spent, resulting from the treatment of straight-run and/or cracked gasoline and/or kerosene fractions of mineral oil, is partially or completely neutralized by means of acid, acid anhydride or acid reacting salt to spring the "acid oil." The "acid oils" which we have found to be efficacious as inhibitors are those sprung from used aqueous alkali solutions resulting from the treatment of petroleum distillates containing phenolic bodies such as phenol, cresol, polyhydroxy benzene ring compounds and thiocresols, as well as sulfur compounds such as mercaptans. Extraction of distillates with aqueous solutions of sodium or potassium hydroxide results in the removal of the aforesaid compounds from the distillate in the form of the alkali metal reaction compound dissolved in the caustic alkali solution. As used in the claims "acid oil" shall mean the product just described.

In addition to the aforesaid compounds, the acid oil may contain low boiling fatty acids such as formic, acetic and propionic, as well as naphthenic acids which were present in the petroleum distillate. The low-boiling acids are harmful in that they cause corrosion of steam turbines and

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therefore these acids must be removed from the acid oil. The removal of the corrosive acids may be accomplished in several ways. For example, in the neutralization of the spent caustic solution, the neutralization may be regulated so that addition of acid to the spent alkali is stopped when the pH value of the solution reaches 8. At pH of 8, acid oil separates from the spent caustic solution which contains the desirable inhibiting constituents while the undesirable corrosive compounds remain in the aqueous phase.

Instead of partially neutralizing the spent alkali solution, it may be completely neutralized with sulfuric or other acidic material to spring all the acid oil from the solution and the total acid oil may be carefully neutralized with alkali such as sodium or potassium hydroxide or carbonate until a pH of 8 is reached. The portion of the acid oil which does not go into aqueous solution is retained as the desired inhibitor.

The corrosive acids can also be eliminated from the acid oil by thorough washing with water. The corrosive acids are more soluble in water than are the desirable inhibiting compounds in the acid oil. Where water washing is relied upon to remove the corrosive acids, the proportion of water to acid oil may vary from 5 to 50 volumes of water to one volume of acid oil and washing is preferably carried out in a multiple stage operation.

Another method for removing corrosive acids from the acid oil is to distill the acid oil at a temperature up to approximately 175° C. At this temperature the low boiling acids, such as formic, acetic and propionic acids distill overhead without any substantial loss of oxidation and rust inhibiting compounds. The residue may then be washed with water.

Acid oil, free of readily water soluble corrosive acids, may be used as such in small amounts in mineral oil. However, unless the acid oil is treated as hereinafter described, it may cause resin-like deposits to form on the surfaces which it contacts. In order to avoid the possibility of resin deposition, we extract the acid oil with a light water immiscible solvent such as hexane, benzene, and light petroleum naphtha in which the acid oil is soluble and which has a boiling point sufficiently low to enable it to be readily removed from the acid oil by distillation. The ratio of acid oil to solvent used in the extraction may vary over wide limits. We have found a ratio of one volume of acid to from one to three to five volumes of solvent to be satisfactory. The resulting extracted acid oil, after removal of the sol-

vent, may be added to mineral oil in amounts of from about .05 to 2% by volume of the oil. The resulting oil should be permitted to stand for a period of several hours or more since a precipitate sometimes forms which should be removed by decantation, filtering and/or centrifuging before using the oil.

In order to demonstrate the utility of our invention, spent caustic soda resulting from the treatment of a blend of straight-run and cracked gasoline from a high pressure thermal cracking operation with aqueous caustic soda solution containing approximately 10% by weight of sodium hydroxide was neutralized with concentrated sulfuric acid until the pH of the solution was 8. An acid oil separated which was extracted with three volumes of hexane. Five-tenths per cent by volume of the resulting acid oil was added to Mid-Continent neutral mineral oil having the following characteristics.

Table I

Viscosity, Saybolt, at 100° F	300–310
Pour point	25° F. maximum
Color N. P. A	2½ maximum
Demulsibility at 130° F	1250 minimum
Demulsibility at 100° F	1500 minimum

Another sample was made in the same manner containing .1% of the acid oil. The two blends were subjected to the Brown-Boveri oxidation test and the following results obtained.

Table II

Sample	Sludge, mg.
Mineral oil (without acid oil)	55.7
Mineral oil plus .5% acid oil	28.5
Mineral oil plus .1% acid oil	25.2

The sample containing .5% by volume of acid oil was subjected to the tentative A. S. T. M. method D–665–42T for testing rust preventing characteristics of steam turbine oil in the presence of water. This method is published in A. S. T. M. Standards on Petroleum Products and Lubricants for October 19, 1942. A test strip was obtained which had a rating of 5—. A perfect strip would have a rating of 5. The test was conducted over a period of 48 hours. No water separated from the oil at the conclusion of the test and the oil was clear.

A Brown-Boveri oxidation test was made on the same oil containing .1% by volume of the acid oil made as aforesaid with the exception that it was not extracted with hexane. A comparison of the results of the oil with and without inhibitor are given in the following table.

Table III

Sample	Sludge	NPA color		Neut. No. after test
		Before test	After test	
Mineral oil (without acid oil)	55.7	+3	Too dark	0.26
Mineral oil (plus 0.1% by wt. of acid oil)	8.0	+3	+8	0.19

Although the acid oil without hexane extraction appears to be a better oxidation inhibitor than the acid oil after hexane extraction, it was less desirable because it caused a resin-like deposit to form on the test strip. This objectionable feature is obviated by the extraction.

Although the acid oil prepared in accordance with the method just described did not include a step of water washing, we prefer to water wash the acid oil. In our preferred method, the acid oil resulting from neutralization to pH of 8 is dispersed in approximately two volumes of water and the aqueous solution is then neutralized to pH of 7 and extracted with a water immiscible solvent such as those previously set forth. The desired inhibitor will be extracted in the form of a solution in the solvent from which the solvent can be removed by distillation and/or fractionation.

It is to be understood that our invention is not limited to the inhibition of the specific oil used in the tests but is applicable in general to various types of steam turbine oils and steam turbines. It should be understood that the inhibitor can be prepared from spent aqueous and alcoholic alkali metal hydroxide solutions.

We claim:

1. The method of preparing an oxidation and rust inhibitor for mineral turbine oils comprising recovering from used aqueous caustic alkali solution resulting from the treatment of low-boiling hydrocarbon distillates containing sulfur and phenolic compounds with aqueous caustic alkali solution, by neutralization with an acidic substance the entire portion of "acid oil" substantially free from constituents soluble in aqueous solution of approximately pH 8, extracting said portion of the "acid oil" with a hydrocarbon solvent boiling below the boiling range of the extractable portion of the "acid oil" and separating the extract from the solvent.

2. The method in accordance with claim 1 in which the solvent is hexane.

3. The method in accordance with claim 1 in which said portion of "acid oil" is dispersed in water, the aqueous dispersion neutralized with acid to a pH of 7 and the resulting dispersion extracted with the hydrocarbon solvent.

4. Method in accordance with claim 1 in which the used caustic alkali solution is neutralized in the presence of water to a point where the aqueous solution has a pH of approximately 8, and the "acid oil" which separates is extracted with the hydrocarbon solvent.

5. Method in accordance with claim 1 in which the used caustic alkali is completely neutralized, the separated "acid oil" is then neutralized with alkali in the presence of water until the aqueous layer has a pH of approximately 8 and the resulting "acid oil" is extracted with the hydrocarbon solvent.

6. Method in accordance with claim 1 in which the constituents soluble in aqueous solution of pH 8 are removed from the "acid oil" by distilling it at a temperature of approximately 175° F. and then washing the residue with water.

7. The method in accordance with claim 1 in which the "acid oil" is washed with water prior to extraction with the hydrocarbon solvent.

8. A mineral turbine oil containing a small amount of the entire portion of "acid oil" soluble in 10% aqueous sodium hydroxide solution substantially insoluble in aqueous solution having a pH of 8 and completely soluble in hexane, the amount of "acid oil" present in the mineral oil being sufficient to inhibit deterioration of the oil and inhibit rusting of steam turbines when the oil is used for lubrication thereof.

9. Mineral oil in accordance with claim 8 in which the amount of "acid oil" contained therein ranges from approximately .05% to 2% by volume.

10. The method of preventing rusting of steam turbines which comprises lubricating the turbines with a mineral lubricating oil containing a small amount of the entire portion of "acid oil" soluble in 10% aqueous sodium hydroxide solution substantially insoluble in aqueous solution of pH 8 and completely soluble in hexane, the amount of "acid oil" present in the mineral oil being sufficient to inhibit deterioration of the oil and to inhibit rusting of steam turbines when the oil is used for lubrication thereof.

11. The method of preparing an oxidation and rust inhibitor which comprises washing a mixture of straight run and cracked gasoline containing sulfur, phenolic and other acidic compounds, with aqueous alkali solution of approximately 10% by weight concentration, neutralizing the resulting alkali solution with an acidic reagent until the aqueous layer has a pH of 8, separating "acid oil" from the aqueous layer, extracting the

entire resulting "acid oil" with approximately 3 volumes of hexane and separating the extract from the hexane.

12. The method of preparing an oxidation and rust inhibitor comprising washing gasoline distillate, containing sulfur compounds, phenolic compounds and other acidic compounds, with aqueous caustic alkali solution, neutralizing the resulting alkali solution with an acidic reagent in the presence of water to a point where the aqueous layer has a pH of approximately 8, separating "acid oil" from the aqueous layer, dispersing the entire resulting "acid oil" in water and neutralizing the dispersion until the water layer has a pH of 7, extracting the resulting oily layer with a hydrocarbon solvent having a boiling point below the boiling range of the oily layer and separating the extract from the solvent.

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