Patented Nov. 13, 1945 2,389,110

UNITED STATES PATENT OFFICE

2,389,110

HYDROCARBON OIL COMPOSITION

Elmer W. Cook, New York, N. Y., and William D. Thomas, Jr., Stamford, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application October 30, 1942, Serial No. 463,944

4 Claims. (Cl. 252—34)

This invention relates to improvements in hydrocarbon oils. More specifically it relates to lubricating oils particularly useful as turbine oils and slushing oils, etc., because of their lubricating, anti-corrosion, film-forming and other unique properties.

The lubrication of the bearings, governing mechanism and other parts of modern steam turbines is usually accomplished by means of a force-feed system which includes the necessary piping, pump, settling tank or centrifuge, filter, cooler, etc., to circulate the oil and to collect and remove contaminating materials. In such systems the oil is subjected to continuous changes in temperature in its flow from the bearings to the cooler. It also is generally contaminated with water from leakage of steam into the system and under these conditions of temperature, moisture, and exposure to air is liable to deteriorate with the formation of acidic oxidation products. This is particularly true in the case of the highly refined oils and white oils commonly employed in turbine lubrication. The acidic oxidation products, water, air, etc., in the system contact the metal surfaces corroding them and resulting in the formation of metal salts and oxides which increase the tendency of the oil to form stable emulsions with the water therein. Since the effective life of a turbine oil is ended when it tends to form emulsions of excessive stability, it will be seen that prevention of oxidation of the oil and corrosion of the metal surfaces of the turbine is an essential requirement.

Although every effort is made to prevent the entrance of water into the circulating system and efforts are made to remove it as fast as it enters some water will ordinarily be present in the turbine oil at all times. Since metal surfaces are preferentially wet with water rather than oil even small amounts of water will collect on the metal surfaces and corrode these parts with the formation of undesirable salts and oxides.

One of the objects of the present invention is, therefore, to provide an oil which prevents preferential wetting of metal surfaces with water. Another object is the prevention of corrosion of metal parts by the combined action of air and moisture. Another object of the invention is to reduce the tendency of the oil to oxidize with the formation of acidic products. Still another object of the invention is to provide turbine oils with decreased tendency to form stable oil-water emulsions. A still further object of the invention is to provide a lubricating oil which accomplishes the aforesaid objects and retains these advantages even after extended use. These objects and others which will be apparent and from what is said hereinafter are accomplished by us by providing a lubricating oil containing an alkyl amine and an alkyl phenol of the kind and in the proportions hereinafter set forth.

Although the use of certain amines in lubricating oil has been proposed to reduce corrosion most of the amines which have been suggested are unsuitable in turbine oils. As pointed out hereinabove the water leaking into the turbine lubricating system is ordinarily collected and removed. Most of the amines suggested for use in lubricating oil heretofore have been water-soluble and obviously when used in turbine oils are extracted from the oil by the water and are removed from the system with it. The higher alkyl amines such as those having 16 to 18 carbon atoms in the alkyl groups are extremely water-insoluble but are also difficultly oil-soluble. Although these higher amines may be dissolved in a refined oil by heating this property of oil-insolubility has discouraged their use since they come out of the oil when it is cooled down to room temperature and in the cooling system of a turbine circulation system.

We have discovered, however, that when primary alkyl amines containing 16 to 18 carbon atoms in the alkyl group are mixed with alkyl phenols the two apparently react forming an addition salt which is highly soluble in the lubricating oil. This enables us to dissolve the higher alkyl amines in lubricating oils with a minimum of effort and after the composition is dissolved in the oil it remains soluble therein even though the oil is cooled below freezing. For example, a 2.5% solution of octadecyl amine in a highly refined Pennsylvania oil SAE grade No. 20 prepared by heating and stirring octadecyl amine with the oil until fully dissolved became cloudy from the precipitation of the amine when cooled to room temperature. On the other hand a sample of the same oil containing 2.5% by weight of octadecyl amine and 2.5% by weight of 2,4-diamyl phenol remained perfectly clear even though cooled to as low as —6° C.

Despite the fact that the alkyl amines and the alkyl phenol form an oil-soluble salt we have discovered that the salt is more effective in preventing corrosion, oxidation, and promoting film-formation than either of the two components alone. This surprising discovery enables us to provide lubricating oils particularly useful in the lubrication of steam turbines having all

the advantageous characteristics hereinbefore set forth.

The alkyl amine-alkyl phenol salt in our improved hydrocarbon oil composition is heteropolar in character and the polar portion of the molecule attaches itself readily to metal surfaces. The non-polar portion of the molecule is hydrophobic and tends to repel water and attract hydrocarbon oil. This action results in the formation of a thin film of oil on the metal surface. For example, when a polished steel specimen covered with drops of water was immersed in oil containing a small percentage of the alkyl amine-alkyl phenol salt it was found that the water was replaced by a thin film of oil.

The alkyl amine-alkyl phenol salt being also highly water-insoluble is not washed away from the metal surface by the action of water in the oil. The weakly alkaline nature of the salt also helps it to reduce corrosion. The salt also shows the anti-oxidant effects characteristic of phenols and thus tends to inhibit the oxidation of the oil circulating in the system. It will be seen, therefore, that this combination of characteristics is highly advantageous in lubricating oils for use in steam turbines.

The effectiveness of our new lubricating oil composition may be illustrated by means of the following test in which the corrosion-inhibiting effects of the composition are clearly shown. This test was as follows: a 400 ml. tall-form beaker containing 200 g. of the lubricant to be tested was mounted on a steam bath, a stainless-steel stirrer was placed so that the blades were ½'' from the bottom of the beaker. A highly polished cold rolled steel specimen, 4.5'' long and having a diameter of $\frac{7}{16}$'' was immersed in the lubricant to a depth of approximately 2''. After stirring the lubricant for 10 minutes 4 ml. (2%) of water was added and the stirring continued. The specimen was examined ½ hour after the addition of water for the formation of brown rust spots and pitting. The temperature of the oil was then raised to 50° C. and the test continued. Periodic examinations were made at ½ hour intervals.

The results shown in the following table were obtained by comparing two lubricating oil samples one of which contained 0.1% of a mixture of equal parts by weight of octadecyl amine and 2,4-diamyl phenol dissolved in a highly refined Pennsylvania oil SAE–20. The other sample containing no additive was used as a control.

Table

	Time, min.	Remarks	
		Control	Oil+additive
Specimen immersed..	0	No film formation.	Film formed on metal surface immediately.
2% water added.....	10		
	40	Brown rust spots, chiefly at surface level.	No corrosion.
Temperature raised to 50° C.	40		
	70	Much corrosion and pitting over entire surface.	Do.
	190	----------	Do.

The alkyl amines which we employ are as stated above, primary alkyl amines containing 16 to 18 carbon atoms, inclusive, in the alkyl chain. Although we may use substantially pure amines we ordinarily, for reasons of economy, employ the commercial grades of octadecyl amine, a representative sample of which contained 25% octadecyl amine, 25% hexadecyl amine and 50% octadecenyl amine. It was a light-colored wax-like solid having a melting point of about 45° C., a boiling point of 300 to 350° C., difficultly soluble in hydrocarbon oils and totally insoluble in water. Other alkyl amines of this character having 16 to 18 carbon atoms and which are insoluble in water and difficultly soluble in lubricating oils are also included within the purview of our invention and may be employed by us. Such mixed alkyl amines are indirectly obtained from the fatty acids of animal and vegetable fats and oils and contain both saturated and unsaturated alkyl groups and minor amounts of shorter chain alkyl amines.

The alkyl phenols which we employ are oil-soluble mono-, di- and tri-alkyl phenols such as, for example, octyl phenol, decyl phenol, ethylhexyl phenol, dodecyl phenol, di-amyl phenol, di-octyl phenol, di-ethylhexyl phenol, di-dodecyl phenol, 2,4,6-tritertiary butyl phenol and other oil-soluble straight or branched chain alkyl phenols. We prefer those alkyl phenols having a total of at least 5 carbon atoms in the alkyl chains because of their greater oil solubility.

Ordinarily the alkyl amine and alkyl phenol are employed by us in substantially equal molecular proportions. As commercially available alkyl amines of the type employed by us vary considerably in purity, the amounts thereof employed in proportion to the alkyl phenol will vary somewhat and it is desirable to use a slight excess of the amine over the theoretical quantity required to form a salt with the alkyl phenol employed. An excess of either component will do no harm, however.

The amount of alkyl amine-alkyl phenol salt necessary to give effective results in our new hydrocarbon oil composition is very small ranging from as low as 0.02% to 5.0% by weight based on the total weight of the oil in the composition. The phenol-amine corrosion inhibitor may be used in conjunction with other additives of turbine oils such as antioxidants or oxidation inhibitors if desired.

Although we have described our invention with particular reference to the improvement of turbine oils, it will be understood that it also contemplates the improvement of other hydrocarbon oils intended for other purposes where a film-forming anti-corrosion oil is desirable. As will be seen from the foregoing the alkyl phenol-higher alkyl amine salts attach themselves to metal surfaces forming water insoluble films not easily washed away by water. The film is compatible with oil, however, and results in the metal surface being covered with a thin film of tenaciously held oil. This effect is of particular value in anti-corrosion oils of the slushing oil type and the improvement of these oils is considered by us to be a part of the present invention and embodied in the scope of the appended claims.

We claim:

1. A lubricating oil composition for the lubrication of steam turbines comprising a major proportion of a hydrocarbon lubricating oil and from 0.02 to 5.0% of a water-insoluble mixture of approximately equal parts by weight of a primary alkyl amine having from 16 to 18 carbon atoms and an oil-soluble alkyl phenol.

2. A lubricating oil composition for the lubrication of steam turbines comprising a major proportion of a hydrocarbon lubricating oil and from

0.02 to 5.0% of a water-insoluble mixture of approximately equal parts by weight of octadecyl amine and 2,4-diamyl phenol.

3. A hydrocarbon oil composition for the lubrication of steam turbines containing a major proportion of a hydrocarbon oil and a minor proportion of a water-insoluble, approximately equimolecular mixture of an alkyl amine having from 16–18 carbon atoms and an oil-soluble alkyl phenol.

4. A lubricating oil composition for the lubrication of steam turbines comprising a major proportion of a hydrocarbon lubricating oil and from 0.02 to 5.0% of a water-insoluble, approximately equi-molecular mixture of a primary alkyl amine having from 16–18 carbon atoms and an oil-soluble alkyl phenol.

ELMER W. COOK.
WILLIAM D. THOMAS, JR.