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METHOD OF DECREASING METAL CORROSION

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This invention relates to a process for decreasing corrosion of metals in contact with viscous hydrocarbon oils. More particularly, it relates to the use of relatively stable organic peroxides in lubricating oil to inhibit chemical solution of copper and similarly corrodible metals by lubricating oils so as to decrease the transfer of the dissolved metal to other parts of a machine lubricated by the oils.

Corrosion of lubricated parts of machines and deposition of metallic copper in the form of even sliced film on ferrous parts has been a serious problem in the refrigerator industry because the deposited metal tends to cause seizure of moving parts i. e. tightly fitting sliding parts, and faulty valve action. From the extensive research on this problem, several causes of chemical solution of copper in lubricating oil and its transfer to surfaces of the machine promoting faulty action have been indicated. There is evidence to support the view that lubricating oils having a high Sligh oxidation test, which is a measure of sludge formed by oil exposed to oxygen for a definite period of time at a specific elevated temperature, for example, 392° F., have a relatively high corroding power. Dissolution of copper by oils with high oxidizing tendency has been explained as being due to fatty acids formed by oxidation of the oils, but the oxidation sludge forming tendency or acid content of an oil has been found not to be the sole factor in the corrosion of copper.

There is also some evidence that the presence of sulfur compounds in oils tends to increase their corrosive action. Another possible factor is the presence of moisture. Although previously, an oil was selected as having low copper solubility and plating tendencies on the basis that it was highly refined and had a low Sligh number or sludging property, this method of selection was not found entirely satisfactory. In addition, very highly refined oils may have less lubricating value, are more costly, and in spite of their low Sligh number, still may show high solubility for copper.

For these reasons, the refrigerator industry has adopted a test for copper solubility as a more practical evaluation of an oil. Under this test, a lubricating oil which does not dissolve a specific small amount of copper under the test conditions for 72 hours is considered to have a reasonably low corrosive effect on copper.

An object of this invention is to provide certain chemicals for addition to lubricating oils which have been found to inhibit corrosive action by the oils regardless of whether the lubricating oil has been highly refined and contains no appreciable amount of sulfur compounds or whether the lubricating oil has not been highly refined and retains its original oiliness. In accordance with the present invention, substances which have been found to have excellent inhibiting properties are the relatively stable peroxides, which for the most part are aromatic peroxides, in particular tetralin peroxide.

As a general rule the aliphatic peroxides are unstable and cannot be safely handled nor can they be maintained in the oil under conditions to which the oil is subjected. Some few exceptions exist of aliphatic peroxides which may be used in oils at low temperatures. Triacetone peroxide is one of the more stable aliphatic peroxides. But, in general, the more stable peroxides are aromatic, e. g., naphthalene peroxide, tetralin peroxide, ascaridole, and benzoyl peroxide. Stability, of course, is considered with reference to the conditions under which the compound is employed. With reference to refrigerating compressor lubricants or lubricants used in similar services the peroxides should be substantially stable at temperatures ranging to about 212° F. In some instances, stability to even higher temperatures may be desired. The way in which these inhibitors are employed and the experimental technique by which they are tested for proving their effectiveness will be fully understood from the following description.

A spiral of copper wire was immersed in a test tube filled with the oil to be tested, then kept in an oven at 200° F. Periodically, samples of the oil were removed from the tube and tested for dissolved copper by the "dithizone" method of analysis. This test depends upon the intensity of violet color developed by copper "dithizonate" in carbon tetrachloride solution. After the oil sample containing the immersed copper wire coil of specified size (36 inches of No. 22 copper wire cleaned by sodium cyanide solution followed by successive washing with water then methanol) has been heated at 200° F. for a definite period, one cc. of the oil was analyzed using the following procedure:

Dissolved copper is leached from the withdrawn one cc. sample with a 10% aqueous solution of sulfuric acid. Copper is then extracted from this acid solution with a 0.006% solution of diphenyl thiocarbazone ("dithizone") in carbon tetrachloride. Upon doing this, if an appreciable quantity of copper is present, a color change from green to violet is noted. Excess diphenyl thiocarbazone is removed from the carbon tetrachloride-copper diphenyl thiocarbazone solution with dilute ammonia (5 cc. of concentrated aqua ammonia per liter) and the violet color of the resultant copper diphenyl dicarbazonate solution may then be matched with a standard solution of this compound of known concentration to determine the amount of copper dissolved by the oil. If no appreciable amount of copper is dissolved by the oil, no change of color from green to violet occurs in the "dithizone" solution indicating that less than about 5 mg. per litre (0.005%) of copper was dissolved by the oil tested.

These tests were run under comparable conditions, the test temperature being held as closely constant as possible, exposure to air being avoided, and the "dithizone" reagent being of constant quality by being freshly prepared and kept in dark bottles. The period of heating the test sample in the presence of the copper wire before the dissolved copper concentration was sufficient to give the green to violet color change in the "dithizone" solution was considered the life of the oil. The following table illustrates the relative effectiveness of the various agents added to oils subjected to the foregoing test. Three varieties of lubricating oils were used and the relative inhibiting power of compounds typifying peroxides, amines, and phenols were observed:

Lubricating oil	Color	Sulfur content, percent	0.1% of inhibitor	Life in hours
Highly refined petroleum distillate	White	0.10	----------	27
			Tetralin peroxide	600+
			Diphenyl amine	400
			Beta-naphthol	475
Medium refined petroleum distillate	Pale yellow	0.25	----------	27
			Tetralin peroxide	115
			Benzoyl peroxide	92
			Diphenyl amine	48
			Beta-naphthol	48
Synthetic hydrocarbon lubricant	do	0.08	----------	120
			Tetralin peroxide	173

From the tabulated results it can readily be seen that the organic peroxides are much more effective than the other types of compounds which also showed good inhibiting properties. The effectiveness of tetralin peroxide is preeminent.

Exactly what effect the inhibitors have on the lubricating oils in diminishing the corrosive action of the oils on the metals is difficult to determine. The peroxides, which are compounds containing two oxygen atoms linked together and each being linked to a different carbon atom in a molecule, have hitherto been known as powerful oxidizing agents or pro-oxidants, but in lowering the copper solubility of an oil they appear to confer upon the oil a characteristic which has generally been identified with low sludge forming oils.

Judging from their copper discoloration test, oils which were improved in regard to lower corrosive effects on copper contained no free sulfur, and even some which were so highly refined as to have very low organically combined sulfur contents were also improved in the same respect by the added inhibitor. These results may be interpreted as indicating that the inhibitor lowers both the oxidation of the oil and the deleterious action of any combined sulfur compounds. It is more important to consider the practical fact that the inhibitor decreases the dissolving power of the oil on such metals as copper.

In general, the amount of preferred inhibitors to be used for improving various lubricating oils is seldom outside the limits of 0.02% to 1% by weight. The exact concentration will depend somewhat upon the characteristics of the oil itself. Usually, about 0.1% to 0.5% of the inhibitor is sufficient. Lubricating oils which in service are contacted with parts containing metals having solution tendencies, such as copper, are particularly to be given a lower copper solubility.

These conditions exist commonly in the lubrication of refrigerating compressors and electrical apparatus wherein copper has to be employed because of its high ductility, heat conducting and electricity conducting properties. The lubricants usually employed in these services are straight mineral oil distillates having Saybolt viscosities ranging from about 100 to 400 seconds at 100° F., and preferably refined by usual acid, clay, or selective solvent treatments to improve, primarily, their color and viscosity characteristics; but even the relatively pure synthetic hydrocarbon lubricants are similarly susceptible to improvement against oxidation and attendant corrosiveness as is shown in the table of results. Instead of depending solely on the preferred peroxide inhibitors, other types of oxidation and corrosion inhibitors may be used in combination with very good results. Also, other addition agents may be simultaneously employed, such as, oiliness agents, sludge dispersers, viscosity improving agents, pour point depressants, stabilizing agents, etc. Remarkably good results have been obtained by employing beta-naphthol together with tetralin peroxide, the mixture being more effective than either ingredient separately in lowering corrosion by some lubricating oils. From all indications, the preferred peroxide corrosion inhibitors should be beneficial in counteracting any corrosive tendency in the use of additional agents, such as fatty acid esters or soaps, or sulfur-containing compounds. These considerations are of value in making the peroxide corrosion inhibitors also valuable for improving slushing oils, hydraulic fluids, greases, etc.

This invention is not to be limited by any theoretical explanation presented herein, or by the examples, all of which are given by way of illustration, but only by the following claims which are intended to claim all novelty inherent in this invention.

We claim:

1. The method of decreasing the corrosion of a metal in contact with a lubricant which comprises adding to the lubricant a small amount of a stable oil-soluble organic peroxide inhibitor.

2. The method of decreasing the corrosion of a metal in contact with a hydrocarbon lubricating oil which comprises adding to the oil a small amount of tetralin peroxide.

3. The method of lowering the copper solubility of a lubricating oil which comprises incorporating

about 0.2% to 1% of an aromatic peroxide in the oil.

4. An improved lubricating composition having a slight tendency to corrode metals such as copper comprising a lubricating oil and a small amount of a stable oil-soluble organic peroxide added as a corrosion inhibitor.

5. A refrigerator compressor lubricating oil having low copper corrosion tendencies which comprises a hydrocarbon lubricating oil having a Saybolt viscosity in the range of 100 to 400 seconds at 100° F. and a small amount of an added stable oil-soluble organic peroxide inhibitor.

6. A lubricating oil as described in claim 4 in which tetralin peroxide is said inhibitor.

7. A lubricating oil composition stabilized against copper corrosion tendencies of any organically combined sulfur constituents present and oxidation effects which comprises a major proportion of mineral lubricating oil and a small amount of an added stable oil-soluble organic peroxide inhibitor.

8. A refrigerating compressor lubricating oil having low copper corrosion tendencies which comprises a refined hydrocarbon lubricating oil having a Saybolt viscosity at 100° F. in the range of 100 to 400 seconds and containing no free sulfur and about .1% to .5% of tetralin peroxide.

9. A lubricant comprising a substantial amount of mineral lubricating oil, a small amount of an oxidation inhibitor selected from the group consisting of aromatic amines and phenols, and a small amount of tetralin peroxide.

10. A lubricant comprising essentially a petroleum oil having a life not substantially more than 27 hours before dissolving 0.05% of copper when heated in contact with a copper wire coil substantially as described, said lubricant having added thereto a sufficient amount of a stable oil-soluble organic peroxide corrosion inhibitor to raise the life of the blend to at least about 115 hours.

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