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STABILIZATION OF LUBRICATING GREASES
AGAINST OXIDATION

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1 Claim. (Cl. 252—32)

The present invention is directed to the treatment of lubricating greases to inhibit oxidation thereof. Many greases as, for example, those used to lubricate ball and roller bearings may be kept in storage for relatively long periods prior to being used and, in some cases, this period of storage may be several years. Ordinary greases during storage exhibit a decided tendency to oxidize, and the oxidation products formed in the grease yield chemical entities, including harmful acids which may attack the metal to which the grease is applied for lubrication purposes. Ball and roller bearings which normally should be adequately lubricated for long periods of time, even at the working temperature of approximately 300 to 400° F., in many cases exhibit decided signs of deterioration when lubricated with oxidized greases. The deterioration of the grease may occur not only during storage, but also during use, and this is especially true if the grease is in contact with a metal favoring or catalyzing oxidation as, for example copper or copper lead alloys.

It has been discovered that if a small amount of a phenylene diamine is added to the grease, the latter is stabilized against oxidation for relatively long periods of time. While the amount of phenylene diamine which may be added may vary with different greases according to the amount and character of the soap present and the character of the mineral oil used and other factors, in general it is preferred that the grease have about .05 to .1% of a phenylene diamine present, the upper limit usually being about 2%. Generally, the amount of phenylene diamine present in the grease should be under 1%.

It has also been discovered that most satisfactory results are obtained if the grease is maintained neutral or slightly basic. If the grease is acid, some of the phenylene diamine oxidation-inhibitor may react with the free fatty acid present in the grease and not only reduce the effectiveness of the inhibitor, but may form compounds which in some cases adversely affect the lubricating characteristics of the grease.

It has also been discovered that the phenylene diamines are soluble in lubricating greases in amounts varying between .01 to .1% based on the weight of the grease, and further it has been found that these small amounts are sufficient to inhibit or retard oxidation.

It has also been ascertained that certain lubricating greases may be beneficially stabilized against oxidation by having more than .1% of a phenylene diamine present. The discovery has

been made that it is not only the phenylene diamine which goes into solution in the grease which is effective to promote and achieve stabilization, but that undissolved phenylene diamine dispersed through the lubricating grease also effects stabilization. More specifically, when the amount of phenylene diamine in the grease exceeds approximately .1% based on the weight of the lubricating grease, then it is desirable to disperse the phenylene diamine in the grease. Any suitable dispersion agent may be used, but it has been found that alcohol, the ethanolamines, and particularly tri-ethanolamine and Butyl Carbitol function very satisfactorily as dispersion agents. In some cases, it is advantageous to dissolve the ethanolamine in the grease up to the saturation point of the grease for the phenylene diamine, and then disperse the remainder of the phenylene diamine through the grease, any of the usual dispersion agents being used. When the grease or a fluid lubricating medium having present a soap contains both dissolved phenylene diamine and dispersed phenylene diamine, it is highly advantageous to maintain the lubricating medium either neutral or slightly basic.

The present invention is applicable to greases containing petroleum hydrocarbons and especially the Pennsylvania mineral oils, Mid-Continent oils, and the Gulf Coastal crudes. For some reason at present not fully known, more effective stabilization with a phenylene diamine, and particularly in quantities of about .1% is found to occur in greases made with paraffin oils. While beneficial results are obtained with greases which are made with coastal oils, the phenylene diamine is not quite as active as in the greases which have been made with paraffin base oils.

It is desired to point out that the phenylene diamines are single ring compounds having a benzene nucleus to which are attached two amino groups. The ortho, meta, and para compounds are known and any of these compounds or mixtures of any thereof may be used in carrying out the present invention. The meta and para compounds have been found to be in general more effective than the ortho, but the choice of the particular member of the phenylene diamine group is governed by the nature of the base oil present in the grease, the additives which may be present therein, and to some extent by the physical characteristics of the phenylene diamines themselves. o-Phenylene diamine is a colorless solid melting at 102° C., and boiling at 252° C.; m-phenylene diamine is a colorless solid melting at 63° C. and boiling at 287° C.; p-phenyl-

ene diamine is a colorless solid melting at 140° C. and boiling at 267° C. All of these phenylene diamines are sparingly soluble in the mineral oil constituent of the grease. The meta and para phenylene diamines are usually preferred in carrying out the present invention.

It is desired to state that the oxidation resistance of greases is determined in the laboratory by employing what is known as the "Norma Hoffman" oxidation test. This is an accelerated test which greatly assists in determining what will actually occur when the grease or other lubricating mediums are used in field operation.

The apparatus employed usually consists of a container having present an oxygen filled bomb containing small trays of the grease to be tested. The container has present an oil bath which maintains the bomb at a constant temperature. In order to accelerate the test, the grease may be mixed with copper or copper lead alloy filings, and if desirable, the temperature of the bath can be raised. This will in a measure function also to increase the oxidation effect. When making the test, it is quite customary that there be mixed with the grease about 2½% of copper lead alloy filings or some similar medium which increases the oxidation effect. The temperature at which the container is maintained will vary, but in general should be between 150° to 250° F. For low melting point lime and aluminum base greases, a temperature of about 150° is satisfactory, and for the higher melting point soda base greases, a temperature of about 210° F. is usually used.

The oxygen bomb which is made of stainless steel, and which contains the grease to be tested, is filled with oxygen and when the temperature is stabilized after the bomb has been in the bath for about an hour, the pressure is adjusted to about 110 pounds per square inch. The pressure drop which indicates the oxygen absorption characteristics of the grease is recorded periodically, and in this manner a curve is drawn visualizing the oxygen absorption of the particular grease which is being tested. The point at which the pressure starts to drop rapidly marks the end of the "induction period" of the grease, and is indicative that the grease has begun to rapidly deteriorate. Greases which are not inhibited against oxygen absorption break down very quickly and show an induction period usually under 100 hours, provided metal filings such as copper or copper lead filings have been mixed with the grease. Greases which have been inhibited against oxidation resist absorption of oxygen for long periods of time varying between 500 to 1500 hours, depending on the temperature used in carrying out the test.

In treating greases either for the "Norma Hoffman" oxidation test or for actual use in field operations, it is desirable to dissolve the phenylene diamine in an oil, said oil being first heated and then add the solution of the oil containing the phenylene diamine to the grease. Alternatively, solid phenylene diamine may be added to the grease, said grease being maintained above the melting point of the phenylene diamine, that is from about 135 to 225° F. when using the meta or ortho phenylene diamine. It is preferred not to add the phenylene diamine to the grease above 350° F., since at this temperature some of the phenylene diamine may be evaporated. In general, it may be stated that the heat of the grease melts the phenylene

diamine. The phenylene diamine may be incorporated in the grease by stirring.

Test No. I

The "Norma Hoffman" oxidation test was applied to an aluminum stearate grease made by mixing .9 pound of aluminum stearate with 14.1 pounds of 300 viscosity (100° F. Saybolt Universal) mineral oil. The aluminum stearate was stirred into the oil and the heat was applied slowly until a temperature of 280° F. was reached. Thereafter, 6.8 grams of solid phenylene diamine was added, this being .1% based on the weight of the grease, and the so-treated grease was stirred for about fifteen minutes. The grease was then poured to a depth of three inches in the usual pan and allowed to cool. This grease was subjected to the "Norma Hoffman" oxidation test, the grease containing 2½% of copper lead alloy filings functioning as an oxidation catalyzer, and the temperature at which the test was made was 150° F. The initial oxygen pressure in the treatment bomb was 110 pounds per square inch. The test sample of the grease which had not been stabilized against oxidation showed a pressure drop of 50 pounds in about sixty hours. On the contrary, samples of the grease which had been inhibited with .1% meta-phenylene diamine and para-phenylene diamine, respectively, showed at the end of 360 hours a pressure drop of a little over 2 pounds, indicating that the phenylene diamines function exceedingly well as oxidation inhibitors.

Test No. II

The "Norma Hoffman" oxidation test was applied to a grease containing 24% of sodium soap, mostly sodium stearate, and 75% of mineral oil. This grease was compounded in a kettle as usual, and the grease was stirred as it cooled. At approximately 250° F., .1% of solid phenylene diamine was added and stirred thoroughly into the grease. The heat of the grease melted the phenylene diamine, and the latter was intimately incorporated in the grease. If desired, the phenylene diamine may be dissolved in a carrier or dispersion agent such as alcohol and Butyl Carbitol or any of the ethanolamines, and the resulting dissolved phenylene diamine dispersed through the grease by stirring.

A sample of the grease compounded as above without any phenylene diamine was subjected to the "Norma Hoffman" oxidation test, there being present in the grease 2½% of copper lead alloy filings. The test was made at a temperature of 210° F., and with the grease under a pressure of 110 pounds per square inch. The grease without the phenylene diamine showed a high pressure drop of 32 pounds at the end of 60 hours. The grease which contained .1% of meta-phenylene diamine showed a drop of only 12 pounds at the end of 360 hours.

Test No. III

A lime base grease was prepared by mixing 16% of a lime soap with 82.9% of mineral oil, said grease containing 1% of moisture. Portions of this grease were tested with and without the phenylene diamine inhibitor. The phenylene diamine was incorporated in the grease by dissolving .24 gram of phenylene diamine in 40 grams of a mineral oil, the mineral oil being maintained at 180° F. The mineral oil with the phenylene diamine dissolved therein was added to 200 grams of the lime base grease above set

forth, the grease being maintained at room temperature. The grease was stirred while the phenylene diamine was incorporated thereon. The grease which contained the phenylene diamine was found to be stabilized against oxidation.

While the greases above set forth contained a soap content of 6 to 24%, these percentages are merely illustrative and the soap content may be much greater or considerably less; the soap contents of the greases are by way of illustration, and not by way of limitation. In some cases, the present invention may be applied to semi-fluid textile greases and semi-fluid electric motor greases, said greases usually containing a soap content of less than 1%. It is also desired to point out that small quantities of soap may be introduced into an oil for detergent purposes, as is done in the treatment of Diesel oils. These lubricants are subject to oxidation, and can be materially improved by adding a phenylene diamine thereto.

Illustrative examples have been set forth of lime base grease, aluminum stearate greases, and soda soap greases. The present invention is not limited to greases containing any particular soaps. Lead soap greases, mixtures of lead soap greases with soda soap greases, mixtures of soda soap greases with aluminum soap greases, nickel soap greases, cobalt soap greases, and manganese soap greases may be treated with any of the phenylene diamines herein set forth to inhibit the greases against oxidation.

Nickel abietate, nickel soap of hydrogenated castor oil, cobalt stearate, cobalt soap of hydrogenated castor oil, manganese soaps of abietic acid and of hydrogenated abietic acid, manganese stearate and manganese soap of hydrogenated castor oil were incorporated in percentages less than 1% in a paraffin base mineral oil. These lubricants which are fluid at room temperature were stabilized against oxidation by adding thereto from .05 to .1% of a phenylene diamine.

In general, it may be stated that the soap which may be present in the lubricating grease may vary between $\frac{1}{2}\%$ and 25%.

The Butyl Carbitol which functions as the dispersion agent for phenylene diamine is chemically termed the butyl ether of diethylene glycol. Preferably, the phenylene diamine is dissolved in the butyl ether of diethylene glycol and the solution added to the grease.

What we claim is:

A neutral or slightly basic lubricating grease containing as its principal lubricating constituent a major portion of a mineral oil, said grease having dissolved therein up to its saturation point an oxidation inhibitor comprising phenylene diamine, together with a further quantity of a phenylene diamine oxidation inhibitor dispersed through said grease with an ethanalamine.

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