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## EXTREME PRESSURE LUBRICANT

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This invention relates to lubricants and to a method of preparing the same and more particularly to lubricants having high film strength characteristics.

An object of this invention is to provide an improved method of preparing a stable lubricant containing chemically combined sulfur, chlorine and phosphorus and which possesses superior extreme pressure properties as measured by both the S. A. E. and Timken film strength testing machines.

Still another object is to provide an improved method of preparing a stable, non-corrosive extreme pressure lubricant having uniformly high extreme pressure properties.

A further object is to provide an improved, stable extreme pressure lubricant and lubricant additive containing chemically combined sulfur, chlorine and phosphorus and which possesses superior film strength properties.

Other objects and advantages of the invention will be apparent from the detailed description which follows.

In an application filed December 19, 1935, by William A. Whittier et al., Serial No. 55,200, entitled "Lubricant and method of preparing same," which issued on August 13, 1940, as Patent No. 2,211,306, there is disclosed a method of preparing extreme pressure lubricants of the nature of those prepared in accordance with the aforesaid application wherein the time required to prepare the lubricants is materially diminished and lubricants having more uniformly high film strength characteristics are obtained.

It has now been discovered that fatty bodies such as animal, vegetable and marine fats or fatty oils may be chemically reacted with sulfur halide, preferably sulfur chloride such as sulfur monochloride and phosphorus compounds, under carefully controlled reaction conditions to produce an improved lubricant which is stable, non-corrosive and which has uniform high extreme pressure characteristics.

Suitable fatty bodies include soya bean, lard, menhaden, sperm, cottonseed and castor oils. Oils of low or intermediate unsaturation are preferable to highly unsaturated oils such as linseed or tung oils since the latter have a tendency to polymerize and do not yield products of as good E. P. properties as the former.

To obtain lubricants having uniformly high film strength properties in accordance with this invention, it is necessary that the fatty body be reacted with sulfur halide under carefully controlled reaction conditions and the sulfurized re-

action product thus produced then reacted with phosphorus or phosphorus compound under carefully regulated reaction conditions. Any appreciable deviation from the predetermined conditions in either case produces lubricants of less desirable extreme pressure characteristics or less effective use of raw materials or both.

As a result of a great deal of experimentation it has been found that superior and highly uniform extreme pressure lubricants may be rapidly prepared by reacting not substantially in excess of 15% by weight of sulfur halide based on the weight of fatty body used at temperatures not substantially in excess of 300° F. When quantities substantially in excess of 15% of sulfur halide are used, an undesirable polymerization occurs which increases the viscosity of the product to an undesirable degree and which produces an undesirable reduction of the solubility of the lubricant in mineral oils. There is no critically minimum amount of sulfur halide which may be used, the minimum being determined in a practical manner by the film strength properties required of the finished lubricant. In general it has been found that when the amount of sulfur halide is decreased below 5% by weight, the degree of improvement in film strength properties which results is below that which will economically justify the treatment of the fatty body. The reaction of sulfur chloride with lard oil is strongly exothermic and it has been found that uniform and superior finished products may only be obtained if the mixture of sulfur chloride and lard oil is maintained below 190° F. and preferably at about 145° to 155° F. until the exothermic reaction has subsided. Lower temperatures may be used, but undesirably long reaction periods are then required. An effective manner of achieving the desired result is to carefully regulate the additive of sulfur chloride to lard oil in accordance with the temperature of the mixture, additional sulfur chloride being added as the temperature of the mixture tends to drop below about 145° to 155° F. After the addition of sulfur chloride is completed the temperature of the mixture is raised to approximately 250° to 300° F. and preferably 275° to 300° F. and the mixture held at this temperature for a period of about one to four hours. A shorter heating time than the period indicated generally results in incomplete chemical reaction of the sulfur chloride with fatty body and produces a corrosive finished lubricant and a longer period of heating at this temperature results in loss of chlorine and de-

crease in the ultimate film strength properties of the final product although heating at this temperature for periods of the order of ten hours may be carried out without serious adverse effects. It should be noted that the mixture of fatty body with other reactants is agitated during all periods of reaction. It is advantageous to incorporate mineral oil or other relatively inert diluent with the lard oil prior to reaction with the sulfur chloride in order to cut the viscosity of the reaction product. After the mixture of sulfur chloride and lard oil has been held at reaction temperature for the period of time indicated, the reaction between the sulfur chloride and fatty body is complete. The completion of the reaction may be determined by immersion of a polished copper strip in the reaction mixture for a period of three minutes. No black deposit should form on the strip. The sulfurized fatty body is then preferably cooled to a temperature of about 220° to 230° F. and a small amount of phosphorus or phosphorus compound capable of reacting with the sulfurized oil is added. The amount of phosphorus or phosphorus compound added may be varied between limits which yield approximately 0.03% to 0.5% of phosphorus and preferably from approximately 0.05% to 0.4% by weight of phosphorus in the lubricant composition. In the case of phosphorus sesquisulfide, for example, this is from about 0.05% to 1% or preferably about 0.1% to 0.8% by weight. Phosphorus sesquisulfide has been found to be a particularly effective phosphorus compound and is a preferred material. However, other phosphorus compounds, including halides such as phosphorus trichloride, oxyhalides such as phosphorus oxychloride, sulfides such as phosphorus pentasulfide, oxides such as phosphorus pentoxide, as well as elemental phosphorus and other bi-elemental phosphorus compounds such as tin phosphide, may be used. The mixture of sulfurized fatty body and phosphorus or phosphorus compound is held at elevated temperature of preferably approximately 220° to 230° F. under conditions of constant agitation for a period of approximately 5 hours. Lower temperatures may be used but the time required to complete the reaction is correspondingly increased. If higher temperatures are used, loss of phosphorus due to fuming occurs with resultant variations in the quality of the final lubricant. However, it has been found that if the sulfurized fatty body is held for the required period of time below about 230° F., the product may then be heated above 230° F. without fuming. The absence of substantial fuming at temperatures above 230° F. is an indication of the completion of the reaction between sulfurized fatty body and phosphorus. At the end of this time the phosphorized and sulfurized fatty body will be found to possess unusually high film strength characteristics.

The lubricant as thus prepared is an excellent extreme pressure lubricant and may be used straight, that is, undiluted with mineral oil or other vehicle. However, the properties of the material thus prepared are greatly in excess of the requirements of ordinary extreme pressure lubrication needs and the lubricant may, therefore, be blended with a suitable vehicle such as mineral lubricating oil and the resultant lubricant effectively applied to those mechanical parts requiring an extreme pressure type of lubricant. For purposes of convenience the lubri-

cant consisting of sulfurized and phosphorized fatty body and without the addition of substantial quantities of lubricating oil is referred to as a lubricant base. When the base is used in mineral oil, in which it is soluble in all proportions, it is preferably used in amounts of approximately 15% to 21% by volume based on the total amount of finished lubricant. This range of lubricant base has been found to give most satisfactory extreme pressure properties consistent with the requirements of modern lubrication needs although greater or lesser amounts may be used for particular lubricating problems.

The results in the table indicate the magnitude of the film strength properties of lubricants containing varying proportions of lubricant base prepared by sulfurizing #1 lard oil with approximately 12% by weight of sulfur monochloride, the initial reaction temperature being maintained at 145° to 155° F. and the reaction temperature then raised to 275° to 285° F. for a period of approximately 3 hours. This was followed by the addition of 0.4% by weight of phosphorus sesquisulfide at a temperature of 220° to 230° F. and the mixture maintained at this temperature for a period of approximately 5 hours. In all cases the lubricant base was blended with Gulf Coast type mineral oil to a Saybolt Universal viscosity at 210° F. of 90 to 95.

Table

| Blend No. | Per cent base in blend | Timken test        |                        | S. A. E. test, lbs. pressure at 1,000 R. P. M. |
|-----------|------------------------|--------------------|------------------------|------------------------------------------------|
|           |                        | Lbs. beam arm load | Pressure, lbs./sq. in. |                                                |
| 1.....    | 15                     | 59                 | 30,250                 | 120                                            |
| 2.....    | 16                     | 68                 | 31,750                 | 220                                            |
| 3.....    | 18                     | 68                 | 31,750                 | 300                                            |
| 4.....    | 20                     | 59                 | 32,000                 | 320                                            |
| 5.....    | 21                     | 68                 | 31,750                 | 330                                            |
| 6.....    | 30                     | 77                 | 35,000                 | 340                                            |

It will be noted from the table that blend 1 containing 15% of sulfurized and phosphorized base possesses a very good Timken test but has a rather low S. A. E. test, the S. A. E. test being only 120 pounds. Blend 2 containing 16% of lubricant base showed a slight improvement while blend 3 containing 18% of base showed a substantial improvement in the S. A. E. test, the Timken test remaining about the same. Further increase of the proportion of base up to 30% by volume shows a comparatively small improvement in the S. A. E. and Timken tests in view of the rather large increase in the proportion of lubricant base used.

It is apparent that the reaction of the sulfurized fatty body with phosphorus or phosphorus compound greatly improves the film strength properties of the sulfurized fatty body when a comparison is made between #1 lard oil reacted with 12% by weight of sulfur monochloride and #1 lard oil reacted with 12% of sulfur monochloride and this sulfurized lubricant subsequently reacted with 0.4% by weight of phosphorus sesquisulfide. In the first case where the fatty oil was sulfurized with sulfur monochloride but was not phosphorized, the Timken test was 25 pounds beam arm load and 9,750 pounds per square inch pressure and the S. A. E. test 310 pounds per square inch at 1000 R. P. M. When the same sulfurized lard oil was subsequently reacted with phosphorus sesquisulfide at a temperature of about 220° F., the Timken test was 68 pounds beam arm load and 33,250

pounds pressure and the S. A. E. test 320 pounds. The tests in each case were made on blends containing 18% by volume of lubricant base in Gulf Coast mineral lubricating oil. It is thus seen that reaction of the sulfurized lard oil with phosphorus sesquisulfide increased the Timken beam arm load from 25 to 68 pounds per square inch and increased the pressure which the lubricant would carry from 9,750 pounds to 33,250 pounds. The change in the S. A. E. test, while small, was nevertheless an increase in favor of the product which had been both sulfurized and phosphorized.

The stability of lubricants prepared in accordance with this invention in actual service tests in unusually good, particularly when considered in the light of the unusually high extreme pressure properties. High extreme pressure properties are all too frequently associated with materials which are highly chemically active and, therefore, highly corrosive to the parts lubricated. Actual service tests on lubricant blends, containing 18% of lard oil sulfurized and phosphorized in accordance with this invention, on hypoid gears in standard motor cars show practically no increase in backlash of the gears after thousands of miles of service. Wear tests on laboratory testing machines, such as the Faville-Levally, are also excellent.

An indication of the stability of the lubricants is shown by accelerated heating tests in which samples of the lubricant were heated at 200° F. for 72 hours and the lubricant thus heated, tested on the S. A. E. and Timken machines. No appreciable decrease was noted in the results obtained on the lubricant thus heated. Blowing the lubricant with air at 200° F. likewise has substantially no adverse effect on the extreme pressure properties and causes only a very slight increase in the viscosity.

In a specific example of preparing lubricants in accordance with this invention, 83.02% by weight of #1 lard oil was mixed with 5.66% of 200 viscosity at 100 Gulf Coast neutral oil and a total of 11.32% by weight of sulfur monochloride was added to this mixture with constant stirring at such a rate that the exothermic heat of reaction maintained the temperature of the mixture at about 145° to 155° F. After addition of the sulfur monochloride was completed, external heat was applied and the temperature increased to 275° to 285° F. This required a period of approximately one and one-half hours. The reaction mixture was held at 275° to 285° F. for three hours at the end of which time a polished copper strip immersed for three minutes showed no black deposits. The mixture was cooled to 220° to 230° F. and 0.4% by weight of phosphorus sesquisulfide added, the agitation being continued. This mixture was held at 220° to 230° F. for five hours using constant agitation. At the end of this time the lubricant base was cooled and blended in an amount of 18% by volume with Gulf Coast mineral lubricating oil to a viscosity of 92 seconds at 210° F. Saybolt Universal. This material had a Timken test of 68 pounds beam arm load and 31,750 pounds per square inch pressure. The S. A. E. test at 1000 R. P. M. was 300 pounds. Analysis showed the lubricant base to contain 5.26% of sulfur, 5.34% of chlorine and 0.21% of phosphorus.

While it has been pointed out that the fatty body is to be sulfurized by reacting the fatty body with sulfur halide, it has been found that small amounts of sulfur halide, that is, of the

order of 1% or 2% by weight calculated on a basis of the entire lubricant base, may be substituted with sulfur. However, more uniform results have been obtained when the sulfurizing reagent consisted only of sulfur halide.

Although in all of the examples set forth the lubricant base has been blended with Gulf Coast oils, it is to be understood that the invention is not limited to these specific oils. Any lubricating oil, paraffin, naphthene or mixed base may be used as blending stock, the only limitation being that it have specifications suitable to produce a lubricant of the quality desired.

This invention has been described in connection with specific details of certain embodiments thereof but it is not intended that such details shall be considered as limiting the scope of the invention except insofar as specifically stated in the specification and as set forth in the following claims.

The term "fatty body" as used in the specification and claims includes those esters normally found in vegetable, marine and animal oils and fats, and the corresponding acids.

We claim:

1. The method of preparing a lubricant which comprises chemically reacting not substantially in excess of 15% by weight of sulfur halide with fatty oil at temperatures not substantially in excess of 190° F. until the exothermic heat of reaction has subsided and completing the reaction at temperatures of approximately 250° to 300° F., adding to the sulfurized oil a small amount of a substance selected from the group consisting of phosphorus and phosphorus compounds capable of reacting with the sulfurized fatty oil and heating the mixture to a reactive temperature not substantially in excess of 230° F. until the reaction is completed.
2. The method in accordance with claim 1 where the time required to complete the reaction at a temperature of about 250° to 300° F. is approximately 1 to 4 hours.
3. The method in accordance with claim 1 where the phosphorus compound is phosphorus sesquisulfide and the amount of phosphorus sesquisulfide is between approximately 0.05% to 1% by weight.
4. The method in accordance with claim 1 where the sulfur halide is sulfur monochloride and the amount reacted is not less than approximately 5%.
5. The method in accordance with claim 1 where the temperature of the fatty oil and sulfur halide is maintained at approximately 145° F. to 155° F. until the exothermic heat of reaction has subsided.
6. The method in accordance with claim 1 where the fatty oil is lard oil.
7. The method of preparing a lubricant which comprises mixing between approximately 5% and 15% by weight of sulfur chloride with fatty oil at temperatures not substantially in excess of 155° F., maintaining the mixture not in excess of this temperature until the exothermic reaction is substantially complete and completing the reaction by heating at temperatures of approximately 275° to 300° F. for a period of about 3 hours, adding a small amount of phosphorus sulfide to the sulfurized fatty oil and heating the mixture at a temperature of approximately 220° to 230° F. for a period of about 5 hours.
8. The method in accordance with claim 7 where the fatty oil is lard oil.

9. The method in accordance with claim 7 where the phosphorus sulfide is phosphorus sesquisulfide and the amount of phosphorus sesquisulfide is between approximately 0.1% and 0.8%.

10. The method of preparing a lubricant which comprises reacting from 5 to 15% by weight of sulfur chloride with a fatty body at temperatures not in excess of 190° F. until the reaction has subsided, continuing the reaction at a higher temperature, not substantially in excess of 300° F., sufficient to give a reaction product having a good copper strip corrosion test but below that temperature at which substantial loss of chlorine occurs and phosphorizing the sulfo-chlorinated

fatty body at a temperature not substantially in excess of 230° F.

11. Method in accordance with claim 10 in which the sulfo-chlorinated body is phosphorized at a temperature of approximately 220-230° F.

12. Method in accordance with claim 10 in which the fatty body is an oil of low unsaturation.

13. Method in accordance with claim 10 in which the fatty body is lard oil.

14. Method in accordance with claim 10 in which the fatty body is sperm oil.

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