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HIGH FILM STRENGTH LUBRICANT AND
METHOD OF PREPARING SAMEWilliam A. Whittier, Kenilworth, Ill., assignor to
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20 Claims. (Cl. 252-48)

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

In an application filed December 19, 1935, by William A. Whittier et al., entitled "Lubricant and method of preparing same," and now issued as Patent No. 2,211,306, of August 13, 1940, there is disclosed a method of preparing extreme pressure lubricants from a sulfurized and phosphorized oil base.

One of the objects of this invention is to provide an improved 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 shortened.

Another object is to provide an improved method of preparing a sulfurized and phosphorized extreme pressure lubricant which is non-corrosive and which does not polymerize under working conditions.

Another object is to provide an improved method of preparing a sulfurized and phosphorized lubricant wherein the sulfurizing and phosphorizing operations are simultaneously effected.

Still another object of the invention is to provide an improved extreme pressure lubricant and lubricant additive containing sulfur, phosphorus and chlorine and which not only possesses exceptional film strength characteristics, but which is non-corrosive and remarkably resistant to polymerization and deterioration under actual service conditions.

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

Efforts have been made in the past to simultaneously chemically combined sulfur and phosphorus with fatty bodies such as fatty oils using phosphorus, phosphorus halide, phosphorus sulfide and various other phosphorus containing materials as the phosphorus compounds and sulfur and/or sulfur chloride as the sulfur compounds. In the previous work the usual procedure was to add simultaneously, all of the desired ingredients to fatty oil and heat the entire mixture for varying periods of time and at varying temperatures and at atmospheric and super-atmospheric pressures to obtain a final lubricant. However, under all of these various conditions it was either not possible to chemically combine a sufficient amount of the phosphorus and/or sulfur compounds to obtain the desired extreme pressure properties or when sufficient amounts

were incorporated, a heavy polymerized mass formed which was entirely unsuitable as a lubricant or lubricant additive.

It has now been found that a considerable saving in time may be effected and a superior sulfurized and phosphorized lubricant obtained by treating fatty body with the reaction product of sulfur halide such as sulfur chloride and one or more phosphorus compounds selected from the group consisting of phosphorus trihalide, phosphorus sesqui-sulfide, phosphorus tri-oxide, phosphine and elemental phosphorus. The reaction product of the sulfur halide and phosphorus or phosphorus compound, either with or without any unreacted material which may be present, is chemically combined with the fatty material to form a reaction product having unusual lubricating properties and capable of greatly enhancing the lubricating qualities of other lubricants such as mineral oils.

A description of the preparation of such a lubricant may be briefly outlined as follows:

Elementary phosphorus or a suitable phosphorus compound such as phosphorus sesqui-sulfide is added to sulfur halide with continuous cooling and agitation. An exothermic reaction takes place between the two compounds and cooling is required to inhibit the violence of the reaction. The cooling operation is not absolutely essential, but is advisable, to reduce the hazard of flashing of the phosphorus compound and loss by volatilization of the sulfur halide. In the case of phosphorus tri-halide and sulfur halide, there is no apparent exothermic reaction, the reaction between these compounds requiring the application of heat to bring the temperature to approximately 320° F. Sufficient pressure is required to prevent volatilization of sulfur halide at this temperature. The precise nature of the chemical reaction is not fully known, but it is believed that at least a portion of the phosphorus sesqui-sulfide reacts to form a compound which contains chemically combined phosphorus, halogen and sulfur, free elementary sulfur also being a product of the reaction when the phosphorus compound used is phosphorus sesqui-sulfide. Particularly satisfactory results are obtained when the proportion of sulfur halide to phosphorus or phosphorus compound is such that there is at least three parts by weight of halogen to one part by weight by phosphorus. The reaction product together with any unreacted material, with or without the removal of free sulfur which may be formed during the course of the reaction, is mixed with fatty oil such as

lard oil and chemically reacted therewith at elevated temperature.

In a specific example, 0.4 gram of phosphorus sesqui-sulfide was added to 12 grams of sulfur monochloride with continuous agitation. An exothermic reaction occurred and cooling was employed to maintain the reaction mixture at a temperature not substantially in excess of 200° F. The completion of the reaction may be readily determined by the cessation of evolution of heat of reaction. This generally requires less than fifteen minutes. After the reaction mixture had been cooled to approximately room temperature, most of the sulfur formed as a product of the reaction was removed by filtration. The remaining material was added to 87.6 grams of lard oil at room temperature and the mixture stirred constantly. An exothermic reaction with the lard oil occurred and the temperature of the mixture rose to approximately 200° F. during the first five minutes of agitation. Agitation was continued and heat added from an external source sufficient to maintain the temperature at approximately 220° F. until a satisfactory corrosion test was obtained. The corrosion test consisted of immersion of a polished copper strip in the reaction mixture at reaction temperature for three minutes. A corrosion test is considered satisfactory when no black discoloration or scaling of the copper strip results. The time required to complete the reaction was approximately three hours. Samples were obtained for testing purposes from several separate batches prepared in accordance with the foregoing procedure and in which the cooking periods were two and three hours and the cooking temperatures ranged from 200° F. to 300° F.

Although lubricants prepared in accordance with the foregoing procedure may be used straight, that is, without the admixture of mineral oils, it is generally preferable to use them blended with mineral lubricating oil. The lubricants prepared in accordance with the aforementioned procedure were blended in the amount of 18% of lubricant to 82% of S. A. E. 90 Gulf Coast mineral oil. Tests of these blends are indicated in Table I:

TABLE I

Lubricant base number	Lard oil	S ₂ Cl ₂	P ₄ S ₄	Heating	
				Time	Temperature
	Percent	Percent	Percent	Hours	° F.
5-28.....	87.6	12.0	0.4	3	220-300
5-32.....	87.6	12.0	0.4	2	200
5-33.....	87.6	12.0	0.4	2	250

Lubricant base number	Timken test		S. A. E. test, lbs. at 1000 R. P. M.
	Beam weight, lbs.	Pressure, Lbs./sq. in.	
5-28.....	68	21,500	340
5-32.....	59	21,500	350
5-33.....	59	21,500	320

As indicated in Table I, excellent extreme pressure properties were obtained as shown by both the Timken and S. A. E. tests. These methods of testing high film strength lubricants are well known and are widely used in the industry to indicate extreme pressure properties of lubricants. A description of the procedure used in

these tests may be obtained from any of a number of well known publications.

The data in Table I show the time of heating of the sulfur chloride-phosphorus sesqui-sulfide reaction product with lard oil. In the case of base number 5-28 the temperature during the heating period was controlled at 220° F. for one hour, 250° F. for one hour and at 300° F. for one hour. The general method of preparation of the bases shown in Table I was the same as that described in the discussion immediately preceding Table I.

Although in the foregoing examples particular oils and compounds have been set forth for use in preparing the lubricants, it is to be understood that the invention is not limited to these specific materials. 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. The amount of sulfur halide and phosphorus yielding material used in preparing the base may vary within rather wide limits, but it has been found that from 1.0% to 15.0% and preferably 5.0% to 7.0% of sulfur by weight, calculated on the finished lubricant base, gives particularly satisfactory results. The proportion of sulfur halide to phosphorus or phosphorus compound is preferably such that there are at least three atoms of halogen to each atom of phosphorus. The phosphorus content is preferably from approximately 0.05% to 7% and particularly effective results have been obtained by using from approximately 0.1% to 2.0%. While phosphorus sesqui-sulfide has been used by way of illustration, phosphorus and other phosphorus compounds have also been found to be suitable. In any event, and regardless of the exact quantities of phosphorus and sulfur combined with fatty oils, it is essential in order to prepare a lubricant which is satisfactory from a point of view of extreme pressure characteristics, corrosion and freedom from polymerization under actual service conditions, to heat the sulfur halide-phosphorus compound reaction product with the fatty body for a sufficient period of time to positively chemically combine the reaction product with the fatty material. It is further essential to carefully control the temperature at which the materials are heated in order to prepare a product of the desired film strength characteristics and of uniform quality. The reaction between the sulfur halide and phosphorus containing material is very rapid and goes to completion readily at room temperature in all cases except when the phosphorus compound is phosphorus tri-halide. In this case the temperature required for chemical reaction is about 320° F. The time required for complete reaction is ordinarily about fifteen minutes. Completion of the reaction may be readily determined by the cessation of evolution of exothermic heat, or in the case of phosphorus tri-halide, by testing samples of the reaction mixture for unreacted tri-halide. This may be readily done by hydrolyzing the samples with water. Any phosphorus tri-halide present will hydrolyze to phosphorus acid, the presence of which may be shown by a reducing action on dilute potassium permanganate. Cooling of the reaction mixture for purposes of safety and to prevent loss of components through volatilization is usually advisable, though not essential. It is particularly important that during the addition of the sulfur halide-phosphorus compound reaction product to fatty body, that the

temperature of the reaction mixture be sufficiently high to permit chemical reaction, but not so high as to exceed that temperature at which the phosphorus compound will either appreciably vaporize or cause an undesirable polymerization to occur. This temperature is approximately 350° F. The reaction time may vary considerably, depending upon such factors as temperature and composition of the reactants, composition of the fatty oil and the proportion of materials entering into the reaction. The time usually required is from approximately two to five hours.

Although lard oil was used for preparing the base in the examples set forth, it will be understood that other fatty oil, vegetable, animal, marine oils and waxes such as cottonseed, castor, rapeseed and sperm oil may be substituted in all or in part therefor. Oils of low or intermediate unsaturation are preferable to highly unsaturated oils such as linseed or tung oil since the latter have a tendency to polymerize and not yield products of as good extreme pressure characteristics as the former.

I claim:

1. The method of preparing a lubricant which comprises reacting phosphorus containing material selected from the group consisting of phosphorus tri-halide, phosphorus sesqui-sulfide, phosphorus tri-oxide, phosphine and elemental phosphorus with sulfur halide and reacting the reaction product with fatty body.

2. The method in accordance with claim 1 in which the sulfur halide is sulfur chloride.

3. The method in accordance with claim 1 in which the phosphorus compound is phosphorus sesqui-sulfide.

4. The method in accordance with claim 1 in which the phosphorus compound is phosphine.

5. The method in accordance with claim 1 in which the phosphorus compound is phosphorus tri-halide.

6. The method in accordance with claim 1 in which the phosphorus compound is phosphorus tri-chloride.

7. The method in accordance with claim 1 in which the temperature of the reaction between the fatty body and reaction product is not substantially in excess of 350° F.

8. The method in accordance with claim 1 where the proportion of sulfur halide to phosphorus containing material is such that there are not less than three atoms of halogen to each atom of phosphorus.

9. The method of preparing a lubricant which comprises reacting phosphorus containing material selected from the group consisting of phosphorus tri-halide, phosphorus sesqui-sulfide, phosphorus tri-oxide, phosphine and elemental phosphorus with sulfur halide, and reacting the reaction product with fatty oil at a temperature not substantially in excess of 350° F. until reaction between the materials is completed.

10. The method in accordance with claim 9 in which the sulfur halide is sulfur chloride.

11. The method in accordance with claim 9 in which the phosphorus compound is phosphorus sesqui-sulfide.

12. The method in accordance with claim 9 wherein sufficient sulfur halide is used to give a final product containing from 1% to 15% of sulfur.

13. The method in accordance with claim 9 wherein sufficient phosphorus containing material is used to give a final product containing from 0.05% to 7% of phosphorus.

14. The method in accordance with claim 9 where the time required for the reaction between the reaction product and fatty oil is from two to five hours.

15. A lubricant composition comprising a major portion of mineral lubricating oil and a minor portion of a material which enhances the lubricating quality of the mineral oil and prepared by reacting phosphorus containing material selected from the group consisting of phosphorus tri-halide, phosphorus sesqui-sulfide, phosphorus tri-oxide, phosphine and elemental phosphorus with sulfur halide, reacting the reaction product with fatty body and continuing the reaction at elevated temperature for a sufficient period of time to complete the reaction between the reagents.

16. A lubricant composition in accordance with claim 15 where the phosphorus containing material is phosphorus sesqui-sulfide, the sulfur halide is sulfur chloride and the temperature of reaction between the reaction product and fatty body is not substantially in excess of 350° F.

17. A lubricant composition comprising the product prepared by reacting phosphorus containing material selected from the group consisting of phosphorus tri-halide, phosphorus sesqui-sulfide, phosphorus tri-oxide, phosphine and elemental phosphorus with sulfur halide, reacting the reaction product with fatty body and continuing the reaction at elevated temperature for a sufficient period of time to complete the reaction between the reagents.

18. A lubricant composition in accordance with claim 17 where the phosphorus containing material is phosphorus sesqui-sulfide, the sulfur halide is sulfur chloride and the temperature of reaction between the reaction product and fatty body is not substantially in excess of 350° F.

19. The method in accordance with claim 1 in which the reaction between phosphorus containing material and sulfur halide is carried out at temperatures not substantially in excess of 200° F.

20. Method in accordance with claim 9 in which the proportion of sulfur halide to phosphorus containing material is such that there are not less than three atoms of halogen to each atom of phosphorus.

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