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LUBRICANT AND METHOD OF PREPARING SAME

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This invention relates to lubricants and to the method of preparing the same, but more particularly to lubricants having high extreme pressure characteristics.

In an application by Lawrence M. Henderson Serial No. 55,199, filed December 19, 1935, entitled "Lubricant and method of preparing same," there is disclosed the method of preparing extreme pressure lubricants from a sulfurized-phosphorized oil base. Although oils have been prepared and blended in the manner set forth therein, which have satisfactory extreme pressure characteristics, it has not always been possible to reproduce a base having predetermined E. P. characteristics. Moreover, the lubricants thus prepared do not always exhibit satisfactory corrosive properties when tested with a copper strip for three hours at 212° F. and also have a tendency to form heavy polymers which settled out of the lubricant when it was tested on a Timken testing machine.

One of the objects of this invention is to provide an improved method of preparing E. P. lubricants.

Another object of the invention is to provide an improved method of preparing a sulfurized-phosphorized E. P. base which is non-corrosive and which does not polymerize under working conditions.

Still another object of the invention is to provide an improved E. P. base and lubricant which not only possesses exceptional E. P. characteristics but which is non-corrosive and remarkably resistant to polymerization and deterioration under actual operating conditions.

We have discovered that if a sulfurized fatty oil is phosphorized under proper conditions of time and temperature, a sulfurized and phosphorized base can be prepared which exhibits remarkable stability and will withstand corrosion tests. If a sulfurized fatty oil base is heated with phosphorus or a phosphorus compound above approximately 230° F., phosphorus fumes are liberated with the result that the amount of phosphorus which eventually is combined in the base is less than the amount added. Furthermore, if the sulfurized base and phosphorus compound is not heated for a sufficiently long period of time, the phosphorus is not completely combined and leaves the base corrosive. On the other hand, heating for excessive periods of time and to excessive temperatures should be avoided. It is therefore essential in order to obtain uniform products of satisfactory commercial specifications, to cook the sulfurized base and phosphorus compound at a temperature sufficiently high to insure combination of the phosphorus and base without exceeding the temperature at which phosphorus fumes off.

As an example of one method of preparing lubricants on a laboratory scale in accordance with our invention, a Gulf Coast lubricating oil, having the following properties—

Table I

Gravity, A. P. I.	21/22
Flash point °F.	350/360
Fire point °F.	385/395
Vis. S. U. @ 100° F.	200/210
Vis. S. U. @ 130° F.	100/110
Vis. S. U. @ 210° F.	43/45
Pour point °F.	—20/—25
Color, N. P. A.	2/3
Carbon residue, per cent	.035
Demulsibility @ 180° F.	1620

was mixed with sulfur chloride in the proportions of 5 parts by weight of oil to 0.5 of a part by weight of sulfur chloride. The mixture was then run into 87.1 parts by weight of prime lard oil and the lard oil was vigorously agitated during the addition thereto of the sulfur chloride-oil mixture. The entire mixture was then slowly heated to a temperature of approximately 270° F. and 7.4 parts by weight of finely ground flours of sulfur were added over a period of about 10 minutes. After the addition of the sulfur the

temperature of the mixture was raised to approximately 330° F. and held at this temperature until a copper strip immersed therein for a period of 2 minutes showed no black coating. After heating for a period of approximately 7 hours at a temperature of from 330° to 340° F., the corrosion test was satisfactory. The mixture was continuously agitated during the entire period of heating. The mixture was then cooled rapidly to approximately 150° F. and then permitted to cool slowly to room temperature. The resulting product had a viscosity of from 400 to 500 seconds Saybolt at 210° F.

99.6 parts of the sulfurized base thus prepared were mixed with 0.4 of a part of finely divided phosphorus sesqui-sulfide and heat applied to the mixture while it was continuously agitated. The temperature was raised to approximately 220° F. but not in excess of 230° F. The mixture was heated while being agitated for a period of approximately 5 hours and then allowed to cool. The sulfurized-phosphorized base thus prepared was then blended with Gulf Coast lubricating oils in the proportion of 18% of base by volume to 82% volume of the blending oils so that the resulting product had the following characteristics: Viscosity, Saybolt Universal at 130° F., 1100/1215; viscosity, Saybolt Universal at 210° F., 160/170; pour point °F. (Maximum), 15° F. As blending stocks, Gulf Coast lubricating oils were used, one of which corresponded to that above set forth in connection with the preparation of the sulfurized base, and the other of which had the following specifications:

Table II

Flash point °F.	510/520
Fire point °F.	590/600
Vis. S. U. @ 210° F.	150/165
Pour point °F.	25 Max.
Color, N. P. A.	8 Max.
Carbon residue, per cent	1 Max.

Several batches of oils blended in the manner above set forth were tested on the Timken and Floyd testing machines, and the blends were also tested for corrosion, with the following results shown in the following table:

Table III

Temperature	Time	Timken test, lbs./sq. in.	Floyd test at 225° F. lbs./sq. in. gauge pressure	3-hour corrosion test at 212° F.
	Hours			
220° F.	5	39, 250	No shear	Good.
220° F.	5	41, 750	660	Do.
220° F.	5	39, 750	600	Do.
220° F.	5	35, 000	600	Do.
220° F.	5	38, 850	600	Do.
220° F.	5	43, 750	600	Do.

It was therefore determined that 5 hours was sufficient time for cooking the sulfurized base with the phosphorus sesqui-sulfide in order to obtain a non-corrosive base at a temperature of 220° F. The temperature was kept below 230° F. since above this temperature it was found that the phosphorus fumed off with the result that the amount of phosphorus which remained in the base was not determinable and a wide variation of the final product resulted.

The Floyd machine may be briefly described as follows: A drive shaft is driven by an electric motor. One end of the shaft is recessed to receive a one-quarter inch diameter test shaft. Both shafts have holes drilled therethrough adjacent contiguous ends to permit insertion of a brass shear pin, one-eighth inch in diameter. The other end of the test shaft is mounted in a split bushing, the lower half of which is held stationary. The bushing is one-half inch long and seven-eighths of an inch outside diameter.

A hydraulic press unit is positioned to exert pressure on the upper half of the bushing. The pressure can be varied at will within certain limits. A test box encloses the bushing and the oil to be tested is placed in the box until the shaft is covered without submerging the top bushing.

When the test is being made the test shaft is rotated by the motor and drive shaft and the pressure on the bushing is increased at definite intervals. When the pressure exceeds the film strength of the oil, the test shaft and bushing freeze together, causing the pin to shear.

From data obtained on running thousands of samples of normal mineral lubricating oil which has not been specially treated for E. P. purposes, it has been found that these oils will not withstand two hundred pounds per square inch hydraulic pressure for five minutes. Oils that will withstand three hundred twenty five pounds per square inch for five minutes are regarded as having extreme pressure properties.

In order to calculate the actual load in pounds per square inch on the test specimens, the hydraulic pressure is multiplied by 76.97.

The oil to be tested can be heated to any desired temperature for the test by means of electric resistance element in the oil bath, controlled by a rheostat.

The Timken machine may be briefly described as follows: A one-quarter inch wide ring of carbon steel is fastened on a mandrel which is rotated by an electric motor. A carbon steel block having a flat surface is placed directly beneath the ring and is adapted to be pressed upwardly against the ring by a pivoted lever arm, on one end of which different weights may be hung. The lubricant to be tested is made to flow continuously between the block and ring from a container adapted to be heated by an electric plate. After running the machine for a given period, the test block is removed and the scar produced by the revolving ring, is measured. From the area of the scar the pressure which the lubricant was able to withstand can be calculated.

Further experimentation proved that if the sulfurized base were heated with the phosphorus sesqui-sulfide for a certain period at a temperature below 230° F., the product could then be heated above 230° F. without causing fuming of the phosphorus, and the resulting product would show good corrosion tests. A series of bases were prepared in which the time and temperature were varied as well as the amount of sulfur and phosphorus sesqui-sulfide added, and the results are given in the Table IV. The lubricant tested in each case was blended by blending 18% by volume of the sulfurized-phosphorized base and 82% by volume of the same Gulf Coast oils as were used to prepare the lubricants listed in Table III. The base and oils were blended in suitable proportions to obtain a final product having substantially the same specifications as the product prepared in accordance with the example previously set forth.

Table IV

Percent sulfur	Percent P_4S_3	Heating time in hours at temperature shown								Timken test pressure. lbs./sq. in.
		210°	235°	255°	275°	290°	310°	330°	350°	
7										15,500
7	0.2	2								37,750
7	0.2	2	1							31,500
7	0.2	2	1	1						41,500
7	0.2	2	1	1	1					32,750
7	0.2	2	1	1	1	1				33,250
7	0.2	2	1	1	1	1	1			34,250
7	0.2	2	1	1	1	1	1	1		31,500
7	0.2	2	1	1	1	1	1	1	1	33,000
7										17,400
7	0.4	2								44,150
7	0.4	2	1							36,000
7	0.4	2	1	1						41,750
7	0.4	2	1	1	1					36,750
7	0.4	2	1	1	1	1				36,750
7	0.4	2	1	1	1	1	1			36,000
7	0.4	2	1	1	1	1	1	1		38,750
7	0.4	2	1	1	1	1	1	1	1	26,500
7										17,400
7	0.6	2								30,250
7	0.6	2	1							34,250
7	0.6	2	1	1						44,750
7	0.6	2	1	1	1					38,250
7	0.6	2	1	1	1	1				36,250
7	0.6	2	1	1	1	1	1			42,500
7	0.6	2	1	1	1	1	1	1		39,750
7	0.6	2	1	1	1	1	1	1	1	40,000
5										16,900
5	0.2	2								35,000
5	0.2	2	1							44,250
5	0.2	2	1	1						38,250
5	0.2	2	1	1	1					37,750
5	0.2	2	1	1	1	1				35,750
5	0.2	2	1	1	1	1	1			35,000
5	0.2	2	1	1	1	1	1	1		35,750
5	0.2	2	1	1	1	1	1	1	1	32,750
5	0.4	2								32,750
5	0.4	2	1							44,375
5	0.4	2	1	1						35,575
5	0.4	2	1	1	1					39,750
5	0.4	2	1	1	1	1				39,500
5	0.4	2	1	1	1	1	1			37,750
5	0.4	2	1	1	1	1	1			37,750
5	0.4	2	1	1	1	1	1	1	1	30,250
5	0.6	2								35,000
5	0.6	2	1							31,250
5	0.6	2	1	1						41,750
5	0.6	2	1	1	1					39,750
5	0.6	2	1	1	1	1				33,750
5	0.6	2	1	1	1	1	1			35,000
5	0.6	2	1	1	1	1	1	1		37,750
5	0.6	2	1	1	1	1	1	1	1	36,500
9										14,500
9	0.2	2	1	1						27,500
9	0.4	2	1	1						40,000
9	0.6	2	1	1						33,750
9	0.8	2	1	1						37,250
9	1.0	2	1	1						33,750

Although the bases prepared in which 5% of sulfur was present had E. P. characteristics equal to those of the 7% sulfur base, the base prepared from the former were of rather low viscosity, namely, 100 to 175 seconds at 210° F. The base prepared with 7% of sufur on the other hand, had a viscosity range of 450 to 600 seconds at 210° F. which makes it admirably suited for blending with the particular lubricating oils above mentioned to obtain a lubricant suitable for transmission and differential use in automobiles. It will be apparent therefore that the amount of sulfur used will be determined to some extent by the desired viscosity of the finished base. The viscosity of the finished base will also depend in a large measure on the rate of agitation during cooking and the temperature at which cooking takes place. The viscosity appears to increase directly with the rate of agitation. Viscosity also increases with increase in temperature up to a certain limit, but decreases if the temperature of cooking becomes excessive.

A comparison of Tables III and IV elicits the fact that the lubricants prepared by heating for 5 hours at 220° to 230° F. are equal in quality to those prepared by heating for 2 hours at 210° F. and then gradually raising the temperature. The method of heating at the fixed temperature is therefore preferable to the method of heating at stepped up temperatures since it is simpler for commercial operation although it requires slightly longer time to obtain the same corrosion tests.

It will further appear from Table IV that the lubricants prepared from bases in which 0.4% of phosphorus sesqui-sulfide were used, are practically as good as the bases prepared with 0.6 of 1% phosphorus sesqui-sulfide from a standpoint of E. P. characteristics and are superior insofar as the corrosion test is concerned. A lubricant prepared from a base, which base had been cooked for 5 hours at 210 to 220° F. and in which 7% of sulfur and 0.4% of phosphorus sesqui-sulfide had been used, did not fume until a temperature of 320° F. had been reached. This temperature is sufficiently high to assure stability of the product under working conditions.

In addition to the reasons preferring 0.4% of phosphorus sesqui-sulfide to 0.6%, it was found that the latter had a tendency to polymerize when tested on the Timken machine. Polymerization appeared as a black gummy deposit on the rings and blocks used in the test. The bases containing 0.4% of phosphorus sesqui-sulfide did not exhibit any polymerization.

The limit of accuracy on the Timken machine is within 2000 to 3000 pounds per square inch. The mean average of the tests obtained in Table

III is 39,725 pounds per square inch. The majority of the results obtained are therefore within the limit of experimental error. It will be evident therefore that a sulfurized and phosphorized lubricant having definite E. P. characteristics can be reproduced fairly accurately. Moreover, it is possible to produce a product having a Timken test of 40,000 pounds per square inch or more and which meet all other required specifications satisfactorily.

In addition to the tests before-mentioned and which have been recorded in Tables III and IV, road tests were made on two lubricants made up with 7% sulfur and 0.4% of phosphorus sesqui-sulfide, one of which had been heated for 5 hours at 220° F. and the other of which had been prepared by heating for 2 hours at 210° F., 1 hour at 235° F. and 1 hour at 255° F. The blended lubricants were placed in the transmission and differential of two automobiles. Table V gives the results on the lubricant which had been prepared by stepped heating, before and after the automobile had been driven 15,650 miles.

Table V

Lubricant	Vis./210° F.	Flash	Fire	Pour	Acid No.	Timken test	Remarks
						Pounds	
Fresh oil	168	465	535	+10	1.0	39,250	6-hr. Timken test on used oil gave 0.0007 gram loss in weight of block and ring. Allowable loss is 0.005 gm.
Transmission	163	455	535	−5	2.1	27,500	
Differential	164	460	545	0	1.4		

Table VI gives the results on the lubricant prepared from the base which had been heated for 5 hours at 220° F., before and after the automobile had been run for 6,249 miles.

Table VI

Lubricant	Vis./210° F.	Flash	Fire	Pour	Acid No.	Timken test	Remarks
						Pounds	
Fresh oil	166	465	535	+15	1.2	35,250	6-hr. Timken test on used oil gave 0.0009 gram loss in weight of block and ring. Allowable loss is 0.005 gm.
Transmission	166	450	530	+10	1.8	33,500	
Differential	167	455	535	+10	1.3		

Both oils stood up extremely well under actual running conditions. Even after 15,650 miles the lubricant showed a Timken test in excess of that of most commercial E. P. lubricants.

The 6-hour Timken test shown in Tables V and VI consists in running the lubricant in the machine for 6 hours with a beam load of 33 pounds. The loss in weight of the ring and block used is determined as an indication of the wear. In both cases the used oils gave very little wear in this test. Maximum loss allowed is 0.005 gram, whereas the lubricants tested showed only 15% and 18% of the allowable loss.

The following is a description of the amounts of material and the conditions used in preparing a batch of the E. P. base on a commercial scale. A homogeneous mixture of 570 pounds of Gulf Coast pale oil having a Saybolt Universal viscosity of 200 seconds and a pour point of −20 to −25° F. and 55 pounds of sulfur chloride was prepared in a cold state. This mixture was added to 9,581 pounds of prime lard oil contained in an enclosed steam jacketed kettle. The mixture was heated to 275° F. while being vigorously agitated. At this point the steam was shut off and 814 pounds of flowers of sulfur were sifted into the contents of the kettle over a period of approximately 2 hours. The contents of the kettle were vigorously agitated during this entire period. At the end of the 2-hour period the temperature had dropped to 265° F. The steam was again turned on and the contents of the kettle heated to approximately 300° F. when the steam was turned off. Agitation was continued for a period of approximately 7½ hours after the addition of the sulfur. During this period the temperature rose from 300 to 344° F. during the first 3 hours indicating that an exothermic reaction was taking place. The temperature during the 7½-hour period was not permitted to drop below 320 to 330° F. and it was found that it was unnecessary to use any further heat to maintain this temperature after the mixture had been initially heated to 300° F.

The sulfurized material was then cooled to a temperature of 220 to 230° F. by circulating the material through cooling coils and back to the kettle. When this temperature had been reached, 44 pounds of phosphorus sesqui-sulfide was added slowly over a period of ½ hour of continuous agitation. The steam was again turned on at such times as was necessary to maintain the temperature at 220 to 230° F. After the addition of phosphorus, agitation was continued for a period of approximately 5 hours while the temperature was maintained at 220 to 230° F. At the end of this period the contents of the kettle were immediately cooled to 130° F. by circulation through the exteriorly located cooling coils and pumped to storage.

It is essential that the contents of the kettle be vigorously agitated during the process in order to eliminate hydrogen sulfide and other corrosive materials which form as a result of the process.

The base thus prepared was blended with various lubricating oils in the proportion of about 18% of base to the oil and the various lubricating oils were blended in order to obtain a product of suitable viscosity and pour point.

Although we have set forth particular oils and compounds in the foregoing examples for use in preparing the base and lubricant, 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. Although we have described the use of sulfur chloride and sulfur in preparing the sulfurized base, sulfur or sulfur chloride alone may be used and the specific method and the specific temperatures used may be

varied within certain limits. The amount of sulfur used in preparing the base may vary within rather wide limits, but we have found that from 1 to 10% and preferably 5 to 7% of sulfur by weight based on the sulfurized base, gives satisfactory results.

Although in specific examples we have described the preparation of the phosphorized base by means of phosphorus sesqui-sulfide, it will be understood that 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 amount of phosphorus in the base should not exceed 2% and preferably should be only a fraction of 1%, preferably 0.2 to 0.6% based on the weight of the sulfurized base. Excessive amounts of phosphorus appear to make the base corrosive. It is essential in order to prepare a lubricant which is satisfactory from a point of view of E. P. characteristics, corrosion, and freedom from polymerization under operating conditions, to cook the materials entering into the base for a sufficient period of time to chemically combine the sulfur and phosphorus in the product. It is further essential to control the temperature at which the materials are cooked in order to prepare a product of the desired E. P. characteristics and of uniform quality.

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

What we claim is:

1. The method of preparing a lubricating stock which comprises chemically combining a small amount of sulfur with a fatty body, adding a small amount of phosphorus or phosphorus compound to the sulfurized body and heating the mixture to a reactive temperature not substantially in excess of 230° F. until the reagents have reacted sufficiently to prevent substantial fuming of phosphorus, continuing the heating until the reaction is completed, and cooling the resulting product.

2. Method according to claim 1 in which the phosphorus yielding material is phosphorus sesqui-sulfide.

3. Method according to claim 1 in which the phosphorus yielding material is a halide of phosphorus.

4. Method according to claim 1 in which the phosphorus yielding material is an oxide of phosphorus.

5. The method of preparing a lubricating stock which comprises adding a phosphorus yielding material to a sulfurized fatty body, heating the mixture to a reactive temperature not substantially in excess of 230° F. until reaction between the reagents is completed, and cooling the resulting product.

6. Method according to claim 5 in which the phosphorus yielding material is phosphorus sesqui-sulfide.

7. Method according to claim 5 in which the phosphorus yielding material is a halide of phosphorus.

8. Method according to claim 5 in which the phosphorus yielding material is an oxide of phosphorus.

9. The method of preparing a lubricating stock which comprises adding a small amount of a phosphorus yielding material to a sulfurized lard oil, heating the mixture to a reactive temperature not substantially in excess of 230° F. until reaction between the reagents is completed, and cooling the resulting product.

10. The method of preparing a lubricating stock which comprises adding a small amount of phosphorus sesqui-sulfide to a sulfurized lard oil, heating the mixture to a reactive temperature not in excess of 230° F. until the reaction is completed, and cooling the resulting product.

11. The method of preparing a lubricating stock which comprises adding a small amount of phosphorus sesqui-sulfide to a sulfurized fatty body, heating the mixture to a temperature between approximately 220° to 230° F. for a period of time to complete the reaction between the reagents, and cooling the resulting product.

12. The method of preparing a lubricating stock which comprises adding a small amount of phosphorus yielding material to a sulfurized fatty material, heating the mixture to a reactive temperature not substantially in excess of 230° F., until the mixture no longer fumes when the temperature is raised above 230° F., then gradually increasing the temperature to a point not substantially in excess of 350° F. until the reaction is complete, and cooling the resulting product.

13. Method according to claim 12 in which the phosphorus yielding material is phosphorus sesqui-sulfide.

14. Method according to claim 12 in which the phosphorus yielding material is a sulfide of phosphorus.

15. Method according to claim 12 in which the phosphorus yielding material is an oxyhalide of phosphorus.

16. Method according to claim 12 in which the phosphorus yielding material is a halide of phosphorus.

17. Method according to claim 12 in which the phosphorus yielding material is an oxide of phosphorus.

18. Method in accordance with claim 12 in which the mixture is heated not substantially above 230° F. for a period of approximately two hours.

19. In a process for phosphorizing a material prepared by heating a mixture of mineral oil, fatty oil and sulfur-yielding material to a temperature sufficient to chemically combine the sulfur with the oil, the steps of heating the said material with a phosphorus-yielding material to a temperature not substantially in excess of 230° F. for a period of time sufficient to prevent phosphorus fuming when the temperature is raised to approximately 350° F.

20. Process in accordance with claim 19 in which the oil and sulfur-yielding material to a temperature heated is not substantially in excess of 340° F.

21. Process in accordance with claim 19 in which the prosphorus-yielding material is phosphorus sesqui-sulfide.

22. Process in accordance with claim 19 in which the sulfur-yielding material comprises sulfur and sulfur chloride, the temperature to which the oil and sulfur-yielding material is

heated is not substantially in excess of 340° F., and the phosphorus-yielding material is phosphorus sesqui-sulfide.

23. Method according to claim 19 in which the sulfur yielding material is sulfur and sulfur chloride.

24. Method according to claim 19 in which the quantity of sulfur present in the mixture is approximately 5 to 9%.

25. Method according to claim 19 in which the quantity of sulfur present in the mixture is 5 to 9% and the quantity of phosphorus added in the form of a phosphorus-yielding material is between .11 and .56%.

26. The method of preparing an extreme pressure lubricant stock which comprises mixing a small quantity of sulfur and sulfur chloride with fatty oil, heating the mixture to a temperature not substantially in excess of 340° F. until the sulfur has reacted with the oil to form a product non-corrosive to a copper strip, adding to the sulfurized oil, a small quantity of a phosphorus compound selected from the group consisting of the halides, oxyhalides, sulfides and oxides of phosphorus, and metal phosphides, heating to a temperature not substantially in excess of 230° F. until the product will not fume when the temperature is raised above 230° F., and cooling the resulting product.

27. Method in accordance with claim 26 in which the product after heating to 230° F. for the requisite period of time is further heated to a temperature above 230° F. but not in excess of 350° F. until the phosphorus had completely reacted with the oil.

28. Method in accordance with claim 26 in which the sulfur chloride is mixed with mineral lubricating oil and then added to the fatty oil.

29. Method in accordance with claim 1 where the mixture is heated to reactive temperature for a period of approximately two to nine hours.

30. Method in accordance with claim 1 where the mixture is heated to reactive temperature for a period of approximately four to five hours.

31. Process in accordance with claim 19 where the phosphorus yielding material and sulfur bearing material are heated for a period of approximately two to nine hours.

32. Method in accordance with claim 26 where the sulfurized oil and phosphorus compound are heated for approximately two to nine hours.

33. Method in accordance with claim 26 where the sulfurized oil and phosphorus compound are heated for approximately four to five hours.

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