

UNITED STATES PATENT OFFICE

2,211,231

LUBRICANT AND METHOD OF PREPARING
SAMELawrence M. Henderson, Winnetka, Ill., assignor
to The Pure Oil Company, Chicago, Ill., a cor-
poration of OhioNo Drawing. Application December 19, 1935,
Serial No. 55,199

42 Claims. (Cl. 252—48)

This invention relates to improvements in lubricants, and more particularly to the method of improving extreme pressure characteristics of lubricants and the product resulting therefrom.

5 The necessity for E. P. lubricants has been brought about primarily by the improvement in automotive engineering. The use of hypoid gears in transmission and differentials has created a need for lubricants of high film strength 10 which would remain intact under operating conditions. The nature of the pressure to which a lubricant is subjected in an automobile transmission or differential is of essentially two kinds— (1) rubbing pressure and (2) rolling pressure. 15 Both actions are encountered during engagement of the gears combined in varying degrees.

Many testing machines have been developed to measure the ability of a lubricant to stand up under extreme pressure conditions, such as are experienced in connection with modern automotive gears. Of the numerous machines perhaps the Floyd and the Timken are best known. 20

The Floyd machine may be briefly described as follows: A drive shaft is driven by an electric 25 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. 30 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 35 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.

40 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 45 freeze together, causing the pin to shear.

From data obtained on running thousands of samples of normal mineral lubricating oil which has not been especially treated for E. P. purposes, it has been found that these oils will not with- 50 stand 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.

55 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 5 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 10 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. 15 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 20 of the scar the pressure which the lubricant was able to withstand can be calculated.

It frequently happens that a particular lubricant may appear satisfactory when tested on the Timken machine and show poor E. P. characteristics 25 when tested on the Floyd machine and vice versa. At the present time the Timken test is regarded with more favor than the Floyd test. The lubricants made in accordance with my invention exhibit excellent E. P. characteristics 30 when tested by either method.

One of the objects of my invention is to provide a base material which when added in suitable proportions to lubricating oils will impart thereto E. P. characteristics. 35

Another object of my invention is to provide a lubricant having high E. P. characteristics.

A further object of my invention is to provide a method for preparing a base which will impart 40 high E. P. characteristics to lubricating oils.

A still further object of my invention is to provide a good E. P. lubricant.

Other objects of my invention will be evident from the following detailed description of my process and products resulting therefrom. 45

To accomplish the foregoing objects, I sulfurize and phosphorize an animal, vegetable, or marine oil preferably at elevated temperatures. The oil is preferably one of relatively low unsaturation such as lard oil or cotton-seed oil, and is preferably 50 sulfurized and then phosphorized in two successive steps, but the two may be done simultaneously. The sulfurization may be accomplished by using elemental sulfur or a sulfur compound such as sulfur chloride. Phosphorization is pref- 55

erably accomplished by means of a phosphorus compound such as phosphorus sesqui-sulfide or phosphorus tri-chloride, but elemental phosphorus as well as other phosphorus compounds may be used. The oil or fat to which a small percentage of sulfur or sulfur-compound is added, is heated for a period of time to chemically combine the sulfur with the oil. Phosphorus appears to have a marked tendency to polymerize the unsulfurized oil to a hard black product unless extreme care is exercised, and for that reason it is preferable to sulfurize first. The sulfurized base is then mixed with a relatively small proportion of phosphorus or phosphorus compound and the mixture heated until combination between the sulfurized base and the phosphorus takes place.

The resulting blend was tested on a Floyd machine and gave the following results:

Table 3

Gauge pressure at which pin sheared.....	525#	575#
Temperature.....	140°	101°
Time.....	8'17"	8'31"

Tests were also made at 204°, 202°, and 232° F. In these tests the machine reached the limit of gauge pressure without the pin shearing.

The same base was blended with the same oil in the proportion of, 10 parts of base to 90 parts of oil and the following results were obtained on the Floyd machine:

Table 4

Gauge pressure at which pin sheared.....	475#	425#	500#	550#	575#	600#	600#	600#	600#
Temperature.....	109°	109°	120°	121°	131°	202°	200°	228°	232°
Time.....	7'56"	7'32"	8'50"	8'21"	8'37"	8'50"	8'50"	8'50"	8'50"

20

The resulting base, when added in minor proportions to standard lubricating oil, produces a product having extremely high E. P. characteristics when measured either on the Floyd or Timken machine.

EXAMPLE I

As an example of an E. P. lubricant prepared by simultaneously sulfurizing and phosphorizing an oil base, the following materials were mixed together—

Table 1

	Parts by weight
No.1 lard oil.....	22.5
Castor oil.....	22.5
Linseed oil.....	45
Phosphorus pentasulfide.....	1
Sulfur.....	9

40

EXAMPLE II

In another example, the base was prepared by mixing together the following ingredients:

Table 5

	Parts by weight
No. 1 lard oil.....	22.5
Castor oil.....	22.5
Linseed oil.....	45
Phosphorus pentasulfide.....	.5
Sulfur.....	9.5

and the mixture heated for 2 hours at 425° F. The resulting material was cooled and blended with the same mineral oil given in the first example, in the proportions of 15% of base to 85% of mineral oil. This blend gave the following results on the Floyd machine:

Table 6

Gauge pressure at which pin sheared.....	525#	425#	450#	No shear	475#	575#	No shear	500#	500#
Temperature.....	114°	109°	109°	203°	200°	204°	235°	231°	230°
Time.....	8'9"	7'40"	7'45"		7'50"	8'32"		8'09"	8'03"

45

50

This mixture was then heated to a temperature of from 425° to 450° F. for a period of 2½ hours. The resulting material was cooled and blended in the proportion of 15 parts by weight with 85 parts of Western Bright Stock having the following characteristics:

Table 2

Gravity, A. P. I.....	21/23
Flash, °F.....	530/540
Fire, °F.....	600/610
Viscosity S. U. at 210.....	155/165
Pour, °F.....	Max. 25

60

65

70

75

EXAMPLE III

In a third example the following ingredients were mixed together and heated at 425° F. for a period of 3 hours.

Table 7

	Parts by weight
No. 1 lard oil.....	22.5
Castor oil.....	22.5
Rapeseed oil.....	45
Phosphorus trichloride.....	1
Sulfur.....	9

This base was blended with the same mineral oil given in Example I, in the proportion of 15 parts of base to 85 parts of oil, and the following results were obtained on the Floyd machine:

Table 8

Gauge pressure at which pin sheared.....	550#	600#	450#	600#	600#	550#	600#	600#	600#
Temperature.....	97°	97°	95°	109°	200°	201°	201°	228°	227°
Time.....	8'20"	8'45"	7'41"	8'50"	8'44"	8'28"	8'45"	8'40"	8'49"

70

75

When this base was blended with mineral oil in the proportion 10 parts of base to 90 parts of oil, the following Floyd tests were obtained:

Table 9

Gauge pressure at which pin sheared	525#	375#	425#	475#	575#	600#	600#
Temperature	101°	92°	100°	101°	109°	111°	227°
Time	8'10"	7'16"	7'32"	7'52"	8'35"	8'50"	8'50"

EXAMPLE IV

As a fourth example, a base was prepared by mixing together the following materials and heating them for a period of 8 hours at 330° to 340° F.

Table 10

Parts by weight

Castor oil	20
Prime lard oil	35
Rapeseed oil	36
Sulfur	8
Phosphorus sesqui-sulfide	1

This base was blended with the same mineral oil given in Example I, in the proportion of 10 parts of base to 90 parts of mineral oil. The Floyd tests were as follows:

Table 11

Gauge pressure at which pin sheared	No shear	No shear	200#	No shear	No shear
Temperature	139°	122°	193°	202°	226°
Time			1'30"		

In the foregoing examples the castor oil was used to lower the pour point of the base. The rapeseed oil was used to improve the miscibility of castor oil in mineral oil, and the lard oil, in addition to reacting with the sulfur and phosphorus to form the E. P. base material, was used to prevent gel-formation which is obtained when castor and rapeseed oils are heated alone.

The following description is an example of a preferred method for preparing sulfurized and phosphorized base but is in no way intended to limit the invention to the particular conditions, constituents, or the quantities of the various constituents stated.

To 87.1 parts by weight of prime lard oil was added a homogeneous mixture or solution consisting of 5 parts of Gulf Coast lubricating oil of 200 to 210 Saybolt Universal viscosity at 100° F. and 43 to 45 Saybolt Universal viscosity at 210° F. and 0.5 of a part of sulfur chloride, and the entire mixture was vigorously agitated. The mixture was then slowly heated to a temperature of 270° F. while being agitated, and then 7.4 parts of finely divided flowers of sulfur were added. The addition of the flowers of sulfur took place over a period of about 10 minutes and the temperature of the mixture was maintained at approximately 270° to 280° F.

After addition of the flowers of sulfur, the temperature of the mixture was raised to 330° F. and agitated for a period of approximately 7 hours while the temperature was maintained at from 330° to 340° F. Corrosion tests of the mixture were made from time to time by immersing a polished copper strip therein for 2 minutes. At the end of 7 hours the strip no longer showed a black coating and the cooking of the mixture was discontinued. The 7-hour heating period gave a "peacock" corrosion strip which is satisfactory.

At this point the mixture was cooled rapidly to a temperature of 150° F. and then allowed to cool slowly to room temperature. The base thus pre-

pared had a viscosity of from 400 to 500 seconds Saybolt Universal at 210° F.

The sulfurized base was then phosphorized by adding thereto an amount of finely divided phosphorus sesqui-sulfide ranging from 0.1 to 2% of the sulfurized base. The mixture was cooked for 1 hour at a temperature of approximately 280° F. and then allowed to cool to atmospheric temperature.

A series of tests on the Timken machine were run on lubricating oils to which were added sulfurized and phosphorized lard oil base prepared in the manner just described. Various amounts of sulfur and phosphorus sesqui-sulfide were used in preparing the base. The table given below sets forth the results obtained. The blends were made by adding 18% by volume of the sulfurized and phosphorized base to a Gulf Coast lubricating oil blend having the following specifications: Viscosity Saybolt Universal at 130° F., 1100-1215; viscosity Saybolt Universal at 210° F., 160-170; pour °F. (maximum), +15° F.

Table 12

Percent sulfur base	Percent phosphorus sesqui-sulfide added to base	Viscosity of resulting base at 210° F.	Timken test pressure lbs./sq. in.
9	0.20	331	25,000
9	2.00	339	34,000
7	0.05	206	15,000
7	0.10	206	11,750
7	0.15	206	12,150
7	0.20	206	28,700
5	0.05	109	14,000
5	0.10	109	18,400
5	0.15	109	16,400
5	0.20	109	25,000
5	0.05	162	14,000
5	0.10	162	16,900
5	0.15	162	25,000
5	0.20	162	32,600
5	2.00	160	37,000

It will be apparent from the above table that insofar as the E. P. characteristics of the lubricant are concerned, there is no advantage in increasing the sulfur content of the base in excess of approximately 5% since the base having 5% of sulfur showed a better Timken test than the base having 9% of sulfur. Likewise, it will be apparent that generally speaking, an increase in phosphorus sesqui-sulfide increases the Timken test and that the optimum amount of phosphorus sesqui-sulfide lies somewhere between 0.2 and 2% since the Timken test increases rapidly up to 0.2% whereas increase from 0.2 to 2% is comparatively small.

In preparing the bases listed in the above table, heavy white phosphorus fumes were given off during phosphorization, indicating loss of some phosphorus. This loss accounts for the fact that the Timken tests in the table are somewhat erratic.

A number of Timken tests were also made on lubricants representing various combinations of

the oils and reagents used in preparing the sulfurized and phosphorized lubricant in order to compare the E. P. characteristics thereof with those of the finished sulfurized and phosphorized base lubricant. The results of these tests are given in the following table:

Table 13

	Timken test pressure, lbs./sq. in.	Floyd test gauge pressure, lbs./sq. in.
10 Gulf coast lub. oil. (same as used in Table 12)	8,900	150 @ 194° F.
15 Lub. oil + 18% prime lard oil	11,100	150 @ 225° F.
Lub. oil + 18% sulfurized prime lard oil. (sulfurized as in example)	13,230	150 @ 195° F.
Lub. oil + 18% sulfurized prime lard oil phosphorized with 0.4% of phosphorus sesqui-sulfide	12,950	125 @ 225° F.
Lub. oil blend with 0.4% phosphorus sesqui-sulfide	15,600	350 @ 223° F.
20 Lub. oil + 18% sulfurized prime lard oil and phosphorized with 0.4% phosphorus trichloride	10,250	575 @ 200° F.
Lub. oil + 18% sulfurized prime lard oil phosphorized with 0.4% phosphorus sesqui-sulfide	16,250	550 @ 227° F.
Lub. oil + 18% sulfurized prime lard oil and phosphorized with 0.4% phosphorus trichloride	18,750	175 @ 193° F.
Lub. oil + 18% sulfurized prime lard oil phosphorized with 0.4% phosphorus sesqui-sulfide	30,500	125 @ 225° F.
	32,750	550 @ 199° F.
	39,000	500 @ 230° F.
25	40,000	575 @ 197° F.
		600 @ 229° F.

It is evident from a comparison of the tests on the blends shown above that those made from a sulfurized and phosphorized base are far superior to the other and are the only blends which give satisfactory tests on both the Timken and the Floyd machines.

Although I have disclosed the use of lard oil in the preparation of the base, it will be understood that other fatty oils, vegetable, animal, or marine oils and waxes, such as rapeseed, cotton and sperm oil, may be substituted therefor, or a mixture of the various oils may be used. Oils of lower unsaturation are preferable to oils of high unsaturation such as linseed and tung oils since the latter appear to polymerize in use.

The proportions of the various constituents entering into the finished product may vary over wide limits but it is preferable to keep the sulfur in the base below 10% and the phosphorus below 2%. In place of phosphorus sesqui-sulfide, other phosphorus compounds may be used in preparing the base, such as phosphorus trichloride, phosphorus pentoxide, various phosphides, such as tin phosphide, and in general, elemental phosphorus and bi-elemental phosphorus compounds. The proportion of the base to oil with which it is blended may also vary over wide limits depending upon the viscosity, pour point, and the E. P. characteristics of the finished product desired.

It will be understood that my invention is not limited to any specific conditions of temperature at which the base is prepared but that any suitable temperature at which the sulfur and phosphorus are effectively combined with the oil base, may be used.

What I claim is:

1. The method of preparing lubricating stock which comprises sulfurizing fatty material and then phosphorizing the sulfurized material.
2. The method of preparing lubricating stock which comprises sulfurizing fatty oil and then phosphorizing the sulfurized oil.
3. The method of preparing lubricating stock which comprises chemically combining a relatively small amount of sulfur with a fatty oil and then chemically combining a small amount of phosphorus with the sulfurized oil.
4. The method of preparing an extreme pressure lubricating base which comprises mixing a relatively small amount of sulfur with a non-

drying or semi-drying fatty body, heating the mixture until the sulfur chemically combines with the fatty body, mixing a small amount of phosphorus compound with the sulfurized body and mildly heating the mixture until the phosphorus has entered into chemical combination.

5. The method of preparing an extreme pressure lubricant base which comprises mixing lard oil with sulfur chloride and sulfur, heating the mixture until chemical combination between the sulfur and oil takes place, adding a small amount of phosphorus sesqui-sulfide to the sulfurized oil and heating the mixture for a sufficient period of time to cause the phosphorus to chemically unite with the sulfurized base.

6. The method of preparing an extreme pressure lubricant base which comprises admixing sulfur chloride with a small amount of mineral lubricating oil, adding the mixture to a relatively large quantity of lard oil, heating the mixture with vigorous agitation to a temperature above the melting point of sulfur, adding sulfur to the mixture and heating the mixture to a temperature at which the sulfur combines chemically with the oil, then adding phosphorus sesqui-sulfide to the oil and agitating at sufficient temperature to chemically combine the phosphorus with the sulfurized base.

7. Method in accordance with claim 4 in which an amount of sulfur up to 10% by weight of the fatty body and an amount of phosphorus compound containing from .1 to 2% of phosphorus by weight of the sulfurized body are used.

8. Method in accordance with claim 5 in which the total sulfur mixed with the lard oil is not in excess of 10% of the lard oil and the phosphorus content of the phosphorus sesqui-sulfide ranges from .1 to 2% by weight of the sulfurized oil.

9. Method in accordance with claim 6 in which the sulfur content of the sulfur chloride does not exceed 10% by weight of the oils and the phosphorus content of the phosphorus sesqui-sulfide ranges from .1 to 2% by weight of the sulfurized oil.

10. The method of preparing an extreme pressure lubricating base which comprises mixing a small quantity of phosphorus compound selected from the group consisting of the chlorides and sulfides of phosphorus with a sulfurized fatty oil, heating the mixture to a temperature up to approximately 280° F. in order to cause the phosphorus to combine with the sulfurized fatty oil, continuing the heating until the phosphorus compound has reacted with the sulfurized oil, and then cooling the resulting product.

11. The method of preparing an extreme pressure lubricating base which comprises sulfurizing fatty oil by heating a small quantity of sulfur and sulfur chloride with mineral oil and the fatty oil up to a temperature of approximately 330° F. until the resulting product shows substantially no corrosion to a copper strip, then adding a small amount of a phosphorus compound selected from the group consisting of sulfides and chlorides of phosphorus and heating the mixture to a temperature up to approximately 280° F. in order to cause the phosphorus to react with the sulfurized oil, and cooling the resulting product.

12. Method according to claim 10 in which the phosphorus compound is phosphorus sesqui-sulfide and it is added in amounts of .1 to 2% of the sulfurized material.

13. Method according to claim 11 in which the phosphorus compound is phosphorus sesqui-sulfide and it is added in amounts of .1 to 2% of the sulfurized material.

14. Method in accordance with claim 10 in which the sulfurized fatty oil is prepared by heating the fatty oil with a small amount of sulfur and sulfur chloride to a temperature up to approximately 340° F. until the sulfur has reacted with the fatty oil and the resulting product shows substantially no corrosion to a copper strip.

15. The method of making an extreme pressure lubricating stock which comprises sulfurizing fatty oil and then chemically reacting a bi-elemental phosphorus compound with the sulfurized oil.

16. Method according to claim 15 in which the phosphorus compound is a metal phosphide.

17. Method according to claim 15 in which the oil is sulfurized by heating it with a small quantity of sulfur and sulfur chloride to a temperature sufficient to cause the sulfur to chemically unite with the oil.

18. Method according to claim 15 in which the phosphorus compound is a sulfide of phosphorus.

19. The method of preparing lubricating stock which comprises chemically combining fatty material with sulfur and phosphorus in such proportions that the ratio of combined sulfur to combined phosphorus is greater than the ratio of sulfur to phosphorus in phosphorus pentasulfide, and retaining the sulfur and phosphorus in chemical combination with the fatty material.

20. Method in accordance with claim 19 in which the fatty material is fatty oil.

21. The method of preparing lubricating stock which comprises chemically combining fatty material with sulfur and phosphorus, said sulfur being obtained from the group consisting of elementary sulfur and sulfur halides and retaining sulfur and phosphorus in chemical combination with the fatty material.

22. Method in accordance with claim 21 in which sulfur is obtained from the group consisting of elementary sulfur and sulfur chlorides.

23. Method in accordance with claim 21 in which the fatty material is fatty oil.

24. Method in accordance with claim 21 in which the sulfur is obtained from elementary sulfur.

25. Method in accordance with claim 21 in which the sulfur is obtained from sulfur monochloride.

26. The method of preparing lubricating stock which comprises chemically combining fatty material with sulfur and phosphorus, said sulfur being obtained from the group consisting of elementary sulfur and sulfur halides and said phosphorus from the group consisting of elementary phosphorus, phosphorus sulfide, phosphorus chloride, phosphorus oxide and phosphides and retaining sulfur and phosphorus in chemical combination with the fatty material.

27. Method in accordance with claim 26 in which the fatty material is fatty oil.

28. Method in accordance with claim 26 in which the combined sulfur is obtained from elementary sulfur.

29. Method in accordance with claim 26 in which the combined sulfur is obtained from sulfur monochloride.

30. Method in accordance with claim 26 in which the combined phosphorus is obtained from phosphorus sulfide.

31. Method in accordance with claim 26 in which the combined phosphorus is obtained from phosphorus sesquisulfide.

32. A lubricating stock comprising fatty material in chemical combination with sulfur and phosphorus, said sulfur being obtained from the group consisting of elementary sulfur and sulfur halides.

33. A lubricating stock in accordance with claim 32 in which the sulfur is obtained from the group elementary sulfur and sulfur chlorides.

34. A lubricating stock in accordance with claim 32 in which the sulfur is obtained from elementary sulfur.

35. A lubricating stock in accordance with claim 32 in which the fatty material is fatty oil.

36. A lubricating stock in accordance with claim 32 in which the fatty material is lard oil.

37. A lubricating stock comprising a major portion of mineral lubricating oil and a minor portion of fatty oil, said fatty oil being in chemical combination with sulfur and phosphorus, said sulfur being obtained from the group consisting of elementary sulfur and sulfur halides.

38. A lubricating stock in accordance with claim 37 in which the sulfur is obtained from the group consisting of elementary sulfur and sulfur monochloride.

39. A lubricating stock comprising fatty oil in chemical combination with sulfur and phosphorus in such proportions that the ratio of combined sulfur to combined phosphorus is greater than the ratio of sulfur to phosphorus in phosphorus pentasulfide.

40. A lubricating stock in accordance with claim 39 in which the sulfur does not exceed 10% and the phosphorus does not exceed 2%.

41. An extreme pressure lubricant comprising a major portion of mineral lubricating oil and a minor portion of fatty oil in chemical combination with sulfur and phosphorus in such proportions that the ratio of combined sulfur to combined phosphorus is greater than the ratio of sulfur to phosphorus in phosphorus pentasulfide.

42. A lubricating stock in accordance with claim 41 in which the sulfur does not exceed 10% and the phosphorus does not exceed 2%.

LAWRENCE M. HENDERSON.