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LUBRICATING OIL COMPOSITION CONTAINING PHOSPHORUS SULFIDE HYDROCARBON REACTION PRODUCT

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My invention relates to the manufacture of improved lubricating oils and more particularly relates to imparting extreme pressure properties to lubricating oil compositions in an improved manner. My invention provides an improved oil and phosphorus pentasulfide reaction product as a lubricating oil additive, an improved manufacturing method to obtain the additive and lubricating oil compositions containing the additive which possesses improved extreme pressure properties.

Many reaction products of many organic products of phosphorus, sulfur and chlorine compounds have been proposed and tried as lubricating oil extreme pressure additives. I have investigated a very great number of these products and the associated manufacturing problems. The specification requirements for gear oils are today so rigid that it is very difficult to find an extreme pressure additive which is non-corrosive, suitably compatible with the mineral oil base, which has the required extreme pressure capacities and yet which is low enough in cost that it can be added to the oils in the desired proportion without increasing excessively the cost of the oils. There do not appear to be any general rules distinguishing useful compositions from those lacking in practical utility. On the contrary, I have found that even apparently minor properties of the starting materials and seemingly unimportant conditions of manufacture are critical in producing additives of superior properties. Thus I have found that heavy mineral oil or bright stocks yield reaction products of special value when reacted with phosphorus pentasulfide under particular conditions of reaction and product work-up. I have found that reaction at about 400° to 500° F. for a period of about 10 to 20 hours produces phosphorus and sulfur containing reaction products of highly useful properties from the extreme pressure standpoint. The proportion of phosphorus pentasulfide employed in the reaction should approximate 7 to 17 per cent and advantageously should be held within the range of 7 to 14 per cent for economy of operation and optimum yield of useful phosphorized product. The reaction mixture contains a number of insoluble reaction products which are oil insoluble or may be deleterious in the trial blends. It is essential that these materials be removed advantageously as by filtration or centrifugation. The separation should be performed at elevated temperature but advantageously after cooling to about 150° to 250° F. For a product of real value in lubricating oils, I also have found that it is then necessary to treat the reaction product by steam blowing until the product is substantially free of hydrogen sulfide. Only in this manner have I been able to obtain a phosphorus and sulfur reaction product which is stable, non-corrosive, clear and oil compatible. Pro-sludging and rusting components are largely eliminated, and the useful E. P. life of the blended oil compositions is enhanced.

Processing and equipment costs are minimized, while yields are greatly improved.

When the new additive is blended into mineral oils, it imparts in even very small concentrations extreme pressure capacities. Advantageously, the concentration in finished oils, e. g. gear oils, is within the range of about 1 to 6 per cent. The most useful oils however contain the additive in concentrations of about 2 to 4 per cent. In terms of phosphorus content, I have found about 0.03 to 0.06 weight per cent organically combined phosphorus particularly useful, depending upon the E. P. demand on the lubricant. The sulfur content appears to be negligible and is largely accounted for by organic by-products. The finished gear oils ordinarily contain in addition other chlorine and/or sulfur containing extreme pressure additives, such as chlorinated wax or chlorinated naphthalene, sulfurized sperm oil or sulfurized lard oil and other chlorine and sulfur containing hydrocarbon derivatives as well as other conventional lubricating oil additives, such as poor depressants, anti-foaming agents and the like.

Although other phosphorus reagents such as phosphorus chlorides or oxides have been employed to react with oils, I have found that phosphorus pentasulfide is by far the most satisfactory reagent to employ in preparing extreme pressure type compositions. The phosphorus sulfides and particularly phosphorus pentasulfides react with mineral oils to give many times greater yields of phosphorus containing compositions useful in improving the load carrying capacities of mineral oil blends. Thus a product prepared by reacting 44 parts of phosphorus trichloride with 356 parts of a bright stock at 150° to 180° F. for several hours and steam hydrolyzing gave a product which was not very different from a suspension of phosphoric acid in oil. When the reaction conditions were modified to provide longer time at higher temperature in the presence of an alkylating catalyst, e. g., aluminum chloride, a product was obtained containing only 0.23 phosphorus and less than 0.05 per cent chlorine from 2700 parts of bright stock and 400 parts of phosphorus trichloride, reacted at 200° to 220° F. for 24 hours and steamed and clarified.

I also have found that it is important to employ a relatively heavy oil of high molecular weight range such as a bright stock, that is a residual lubricating oil stock, rather than lighter oils such as neutral oils or the usual lubricating oil distillate stocks, as a starting material. If the reaction is run on neutral oils, a large percentage of insolubles forms during the phosphorus sulfide reaction. After filtration, the liquid portion again forms additional large amounts of insolubles during steam treatment. Yields of phosphorus containing products amount to as little as 25 per cent based on the phosphorus sulfide used. By contrast, with bright stocks, insolubles formation is greatly reduced and the comparable yields of phosphorus containing products range from about 70 to 95 per cent. Moreover, the load capacity of the bright stock reaction products is superior to that of the neutral oil reaction products. For example, where additives prepared according to my invention from bright stocks consistently show less than 30 mgs. total wear on the test cup and block in Timken L–20 procedure #3 weed out tests (see below for test description) without burnish or score, comparative preparations using a neutral oil may show about 90 mgs. or more total wear with observable burnish and scoring. For best results it is advantageous to employ bright stocks having viscosities within the range of about 120 to 300 SUS at 210° F.

Although reaction of phosphorus sulfides with oils com-

mences at comparatively low temperatures, I have found that the temperature level during the reaction period is of fundamental importance in determining yield and the nature of the reaction products. Thus phosphorus pentasulfide reacts with various bright stocks at about 320° F. Only about 2.5 to 7 per cent of phosphorus pentasulfide, however, is reacted in from 10 to 20 hours. The reaction products moreover are not stable under steam treatment. Up to half of the phosphorus increase is hydrolyzed to oil insoluble phosphorus acids. The resulting composition contains an acid haze which is difficult to separate completely by filtering, settling or water washing. The traces of acid left in the composition are pro-rusting, pro-corrosive and pro-sludging. Reaction times up to 48 hours effect little improvement with respect to acid haze on steaming. Also, additional digestion at 320° F. after filtering out unreacted phosphorus pentasulfide or using a reduced amount of phosphorus pentasulfide such as 2.5 per cent for reaction times up to 72 hours does not eliminate the acid haze after steaming. Increase in the reaction temperature up to 360° F. also is ineffective. If the reaction is conducted at 400° to 500° F., however, the products are stable and show no separation of acid haze during the steaming process. In addition, about 2 to 4 times as much phosphorus pentasulfide reacts at 400° to 500° F. so that the final product contains from 3 to 6 times as much oil soluble phosphorus in chemical combination as the low temperature reacted materials.

The reason for the hydrolysis of the low temperature reaction products to insoluble acids during the steaming is not understood. However, it appears that only one of the two available atoms of phosphorus in the molecule of phosphorus pentasulfide is directly alkylated, that is linked to a carbon in a considerable portion of the low temperature reaction products. The second atom of phosphorus is connected to the oil alkylated phosphorus atom only through a sulfur atom. The conditions of the steam treatment are sufficient to remove sulfur from phosphorus, and this action also releases phosphorus in the form of oil insoluble phosphorus acids. When the oil-phosphorus pentasulfide product is formed at 400° to 500° F., both atoms of available phosphorus appear to be directly alkylated or linked to carbon atoms so that hydrolysis resulting in free inorganic phosphorus acids does not occur under the conditions of steam treatment.

The reaction of the oil and phosphorus pentasulfide produces oil insolubles. I have found that it is important to separate solid from liquid products at elevated temperature, e. g. 150° to 250° F., before the steaming operation. This removes products which would be oil soluble after steaming but which are at the same time quite pro-sludging in typical gear oil blends. Thus I have compared preparations reacted to 8, 10, and 12 per cent phosphorus pentasulfide without insolubles separation before steaming and similar preparations which were clarified by hot filtration before steaming. The former were uniformly higher in per cent phosphorus but they were consistently more pro-sludging, showing as high as about 1 per cent sludge and as high as 0.75 per cent tube deposits in sludge accumulation tests at 120 hours. The insolubles separation step appears to be more critical with the lighter stocks as the very heavy stocks form considerably less amount of insolubles during the phosphorus pentasulfide reaction. Separation of the non-liquid products is much more difficult at room temperature and removes a considerable amount of relatively low solubility reaction products without any compensating improvement in the product. Separation at reaction temperatures is mechanically more difficult and less likely to remove all the undesirable components. Accordingly, I prefer to cool the reaction mixture to about 150° to 250° F.

The significance of the steam treating step is illustrated in the following examples and data:

	Steamed—Example 1 (below)		Unsteamed—Example 6 (below)	
Sulfur, percent	1.16		3.72.	
Phosphorus, percent	1.57		1.65.	
Copper Strip, 1 hr. at 250° F.	Light Peacock		Black.	
Reaction with Water	None		Evolves H_2S.	
Odor	Slight Sulfurous		Strong H_2S.	
Homogeneity	Clear		Solids separate at room temperature.	
Rusting of Gear Oil Blends	A	B	C	D
Base Oils, Weight Percent:				
Solvent refined neutral	26	26	26	26.
Solvent refined bright stock.	74	74	74	74.
Additives, Weight Percent:				
Preparations of Above Examples.	4.0	4.0	4.0	4.0.
Sulfurized Sperm Oil, 12% S, percent.	4.5	4.5	4.5	4.5.
Chlorinated Paraffin Wax, 42% Cl, percent.	4.5	4.5	4.5	4.5.
Lauric Acid, percent	0.15		0.15	
Acryloid 150, percent	0.10	0.10	0.10	0.10.
DCF 200, percent	0.005	0.005	0.005	0.005.
CRCL–13 Rust Test	No Rusting.	No Rusting.	Loose Black Coat.	Loose Black Coat.
Gear Oil Proc. Turb. Oil Rust Test.	Perfect	Lt. Film Rust.	do	Do.
Gear Oil Proc. Turb. Oil Rust Test, Continued to 48 hrs.[1]	Peacock Stain.		Hvy. Rust.	
Gear Oil Proc. Turb. Oil Rust Test, Continued to 96 hours.[1]	do			

[1] An additional 2.5 percent H_2O added each 24 hours on test

Thus the product of Example I shows greatly reduced amounts of rusting in typical gear oil blends by CRC L–13 and gear oil procedure turbine oil rusting tests. Compare blends A and B in the above table to blends C and D. This is a very important advantage inasmuch as a major use for extreme pressure additives is in hypoid gear lubricants which are commonly required to operate in the presence of water without rusting. The copper strip test for 1 hour at 250° F. on the steamed product gives a light peacock stain versus a black coat on the unsteamed product indicating less sulfur corrosion. The odor of the steamed product also shows a corresponding improvement. The steamed product is quite stable in the presence of moisture compared to the unsteamed product which gives off quantities of hydrogen sulfide on warming with a small amount of water. The steamed product is also clear and homogeneous compared to a definite haze and separation in the corresponding unsteamed preparations filtered at 150° to 250° F. The steaming step is conducted at elevated temperature, e. g. about 300° F. Further finishing is unnecessary except to insure the desired degree of dehydration. Vacuum at about 300° F. or nitrogen blowing or both effectively dehydrate the concentrates. Air may be blown over the products to remove water but the process is more tedious and air exposure tends to degrade color and increase acidity.

The nature of the products and processing methods of my invention are further illustrated in the following detailed examples of typical preparations in which Examples III (A), VI, and VII represent undesirable or ordinary procedures. Tests on the base oils employed in the examples are listed in Table I below.

Example I (A)

A 22-liter 3-neck flask equipped with a vacuum seal stirrer and a heating mantle was charged with 12,543 grams of base oil "B" and 127 grams of diatomaceous earth filter aid. The oil was heated to 240° F. with stirring under a vacuum of 1–2 cm. of mercury to thoroughly dry the contents. Then 1,394 grams (7 per cent) of phosphorus pentasulfide were added and heating continued. Air was removed from the flask by evacuating. As hydrogen sulfide was evolved from the reaction, the pressure was allowed to build up to atmospheric. This occurred at

275° F. The temperature was raised to 400° F. over a period of 1 hour. Heating and stirring were continued at this temperature for 10.5 hours. Then the preparation was allowed to cool and stand overnight. The following day it was reheated to 250° F. and filtered into a clean 22-liter flask. Then 0.65 gram of Dow Corning Fluid 200 antifoam additive was added and the preparation reheated with stirring. Steam was introduced to the flask at a temperature of 230° F. and the temperature raised to 320° F. in 30 minutes. Steam blowing was continued at approximately this temperature for 4.0 hours. The steam was shut off and the flask gradually evacuated to a pressure of 1–2 cm. in 30 minutes. Heating was continued for an additional 30 minutes. The product was cooled to 260° F. and filtered through paper with no evidence of insolubles or acid haze. Analysis of the product showed: Acid No., 30.9; saponification No., 47.1; sulfur, 1.15 per cent; phosphorus, 1.78 per cent; O. D. color, 1,461; copper strip 1 hour at 250° F., light peacock; insolubles, none.

Example I (B)

This preparation was identical with that of Example I (A). Analysis of the product showed: Acid No., 28.4; saponification No., 51.0; sulfur, 1.02 per cent; phosphorus, 1.51 per cent; O. D. color, 1,653; insolubles, none.

Preparations of Example I (A) and example I (B) were blended in equal proportions for extensive testing and gave the following analysis: Gravity API, 20.5; acid No., 39.1; saponification No., 44.7; sulfur, 1.16 per cent; phosphorus, 1.57 per cent; O. D. color, 1,627.

Example II

A 22-liter 3-neck flask equipped with a stirrer and a heating mantle was charged with 13,960 grams of base oil "B" and 1,280 grams of phosphorus pentasulfide (8.4 per cent). The mixture was heated with vigorous stirring to a temperature of 400° F. in 3 hours. Stirring was continued at this temperature for 10.5 hours and the mixture allowed to cool for 6 hours. Diatomaceous earth filter aid (127 grams) was added and the mixture filtered at 200° to 225° F. into a clean 22-liter flask. Dow Corning Fluid 200 antifoam (0.75 gram) was added and the preparation reheated with stirring. Steam was introduced into the flask at approximately 320° F. for 4½ hours. Then air was introduced over the stirred contents of the flask for 45 minutes to remove water. The product was cooled to approximately 200° F., 152 grams of diatomaceous earth filter aid was added, and the mixture filtered. The product showed the following analysis: Gravity, 20.4; Kinematic viscosity at 210° F., 218.7; Acid No., 10.9; saponification No., 58.1; O. D. color, 1,104; sulfur, 0.98 per cent; phosphorus, 1.92 per cent; insolubles, none.

Example III (A)

A 5-liter 3-neck flask equipped with a vacuum seal stirrer and a heating mantle was charged with 2,580 grams of base oil "B" and 420 grams of phosphorus pentasulfide. Air was removed from the flask by evacuation to approximately 2 cm. mercury pressure. The contents were heated with stirring to 480° F. over a period of 2 hours. Hydrogen sulfide was evolved vigorously at temperatures over 350° F. and was vented off at atmospheric pressure. Stirring was continued at 480° F. for 18 hours and the reaction product cooled to 320° F. before mixing with 30 grams of a diatomaceous earth filter aid (Hy-Flo Supercell). The preparation was filtered at a temperature of 150° to 200° F. A pint of the reaction product at this stage analyzed: Acid No., 37.9; sulfur, 6.2 per cent; phosphorus, 3.78 per cent; copper strip 1 hour at 250° F., black.

Example III (B)

The remainder of the preparation was placed in a clean flask equipped with a stirrer, heater and steam inlet tube. Approximately 0.005 per cent of Dow Corning Fluid 200 antifoam additive (0.12 gram) was added and the contents heated to 260° F. with stirring. Steam was then introduced at a rather rapid rate and the temperature increased to approximately 320° F. over a period of about 15 minutes. Steaming was continued at this temperature for 3 hours. Water was removed from the product by slowly evacuating the flask to below 5 cm. mercury pressure and stirring at 320° F. for 10 minutes. The product was allowed to cool overnight and was then reheated with 15 grams of filter aid. The product filtered at 150–220° F. rather slowly using a Buchner funnel. Analysis of the product gave: Acid No., 65.9; saponification No., 96.2; sulfur, 2.86 per cent; phosphorus, 3.92 per cent; O. D. color, 4,830; copper strip 1 hour at 250° F., light peacock.

Example IV

A 5-liter 3-neck flask equipped with a stirrer and heating mantle was charged with 2,760 grams of a propane de-asphalted dewaxed cylinder stock, base oil "D." The oil was heated to 210–230° F. and nitrogen blown until dry. Then 240 grams of phosphorus pentasulfide was added and the mixture heated with stirring to a temperature of 400° F. over a period of approximately 2 hours. The mixture was stirred at 400° F. for 18 hours. After cooling to approximately 240° F., 1 per cent of filter aid was added and the mixture filtered. This filtered product was placed in a clean flask equipped with a stirrer and 0.15 gram of Dow Corning Fluid 200 antifoam was added. The mixture was heated to 320° F. and then blown with steam at 320–360° F. for 3 hours. The heat was shut off and dry air was passed into the flask over the surface of the stirring product until the temperature dropped to 240° F. The product was filtered through paper in a Buchner funnel. The product gave the following analysis: Acid No., 36; saponification No., 66.7; sulfur, 1.39 per cent; phosphorus, 1.86 per cent.

Example V

A 12-liter 3-neck flask equipped with a stirrer and an electric heating mantle was charged with 6,721 grams of Pennsylvania bright stock, base oil "C," and heated to 310° F. Phosphorus pentasulfide (1,094 grams) was added with stirring and the temperature raised to 440° F. over a period of 1 hour and 15 minutes. Vigorous hydrogen sulfide evolution occurred, gradually stopping almost completely at the end of 7 hours of digestion at approximately 440° F. Heating was continued 3 hours longer and the reaction allowed to stand for 56 hours. The preparation was then reheated to 235° F., mixed with 67 grams of filter aid (Hy Flo Supercell) and filtered. Tests on the product showed: Gravity, 15.9; kinematic viscosity at 130° F., 4,594; kinematic viscosity at 210° F., 144.4; acid No., 52.2; saponification No., 158; O. D. color, 2,750; sulfur, 6.91 per cent; phosphorus, 4.19 per cent (4.06 is theoretical).

This preparation (3,000 grams) and Dow Corning Fluid 200 antifoam (0.15 gram) were placed in a 5-liter flask equipped with a stirrer and steam inlet tube and heated to 250° F. Steam was blown through the mixture with stirring and the temperature raised to 320° F. over a period of 15 minutes. Steaming was continued at approximately this temperature for 4½ hours and the product dried by passing air into the flask above the surface of the stirring mixture for 10 minutes. Tests on the product show: Gravity, 21.1; kinematic viscosity SUS at 130° F., 9,582; kinematic viscosity, SUS at 210° F., 890; acid No., 75; saponification No., 95.4; O. D. color, 1,940; sulfur, 2.07 per cent; phosphorus, 3.67 per cent; cast, dark green.

The Pennsylvania bright stock appears to be generally slightly superior to Midcontinent solvent treated and/or propane deasphalted bright stocks with respect to the total amount of phosphorus pentasulfide (about 17 per cent) which can be reacted without excessive solids precipitating during the reaction. Also the product after

steaming has a considerably better dark green cast. This gives better colored blends than relative O. D. colors might indicate. Economics and available supply however, usually make the solvent treated Midcontinent oils commercially preferable.

Example VI

A 5-liter 3-neck flask equipped with a stirrer and heating mantle was charged with 3,162 grams of base oil "B" and heated to 275° F. Phosphorus pentasulfide (264 grams) was added and the mixture heated with stirring to a temperature of 400° F. over a period of approximately 2½ hours. Heating was continued at 400° F. for 10 hours and the reaction shut down for 6 hours. Diatomaceous earth filter aid (34 grams) was added to the preparation. It was then reheated to 235° F. and filtered. Analysis of this product showed: Gravity API, 21.1; viscosity SUS at 210° F., 175; sulfur, 3.72 per cent; phosphorus, 1.65 per cent; O. D. color, 1,537; copper strip 1 hour at 250° F., black. A heavy haze of insolubles slowly separated on standing at room temperature.

Example VII

A 5-liter 3-neck flask equipped with a stirrer and electric heating mantle was charged with 3,720 grams of base oil "B" and 280 grams of phosphorus pentasulfide. The temperature was raised to 320° F. over a period of approximately 1 hour and heating and stirring were continued at approximately this temperature for 48 hours. The product was cooled to 230° F. 40 grams of a diatomaceous earth filter aid was added and the product filtered. The total solids removed amounted to 85 grams after washing with naphtha. These washed solids were hygroscopic and appeared to contain approximately 45 grams of granular unreacted phosphorus pentasulfide. The filtered portion of the preparation was mixed with 0.005 per cent of Dow Corning Fluid 200 antifoam and reheated with stirring in a clean flask. Steam was blown through the mixture at 320° F. for 2½ hours. The preparation was cooled below 200° F. with stirring and allowed to settle for several days. A small portion of emulsion free clear water layer was removed and gave an acid number of 493. A portion of the emulsified, acid containing product was reheated with stirring to a temperature of 320–330° F. and placed under a vacuum of 10–20 mm. mercury pressure for one hour. A small amount of heavy reddish product separated of very high acid number and phosphorus content. This product was then decanted from the heavy acid layer and filtered through paper. Analysis of this product showed: Acid No., 14.4; saponification No., 33.4; sulfur, 0.72 per cent; phosphorus, 0.84 per cent.

Calculation shows that at least 6 per cent of the 7 per cent of phosphorus pentasulfide used reacted to give an oil soluble reaction product. The theoretical amount of phosphorus in this reaction product is 1.69 per cent. The amount of phosphorus remaining after steaming and nominal clarification is 0.84 per cent indicating 50 per cent hydrolysis to the objectionable insoluble phosphorus acid haze.

Example VIII

A 5-liter 3-neck flask equipped with a stainless steel stirrer and an electric heating mantle was charged with 2,720 grams of Pennsylvania bright stock (base oil "C") and 680 grams of phosphorus pentasulfide. The mixture was heated with stirring to 400° F. and the reaction continued for 36 hours. The preparation was filtered at approximately 250° F. The product gave: Acid No., 40.2; saponification No., 141; sulfur, 9.53 per cent; phosphorus, 4.79 per cent. The product was semi-solid at room temperature.

This yield represents approximately 17 per cent of phosphorus pentasulfide reacted to give a fluid reaction product suitable for steaming. In general, larger amounts appear to go more to solid reaction products rather than fluid products. More concentrated reaction products are possible but the net yield based on phosphorus pentasulfide charged tends to decrease rather rapidly when higher percentages of phosphorus pentasulfide are used.

Tests on the various base oils used in preparation and compounding are tabulated below:

TABLE I

Identity	A	B	C	D
Crude Source	Mid-Cont.	Mid-Cont.	Penn.	Mid-Cont.
Refining Method	Solvent	Solvent	Solvent	Deasphaltin and Dewaxing.
Type	Neutral Oil	Bright Stock	Bright Stock	Cylinder Stock.
Gravity	28.9	25.9	26.3	20.6.
Flash	415	525	570	540.
Fire	465	585	615	625.
Kin. Viscosity SUS at:				
100° F	206	1,949	2,235	5,189.
130° F	105	739	867	
210° F	46.3	121.1	150	197.4.
Kin. Viscosity Index	90	86	103	75.
Pour	10	0	10	15.
Color	2+	6−	8−	O. D. 2940.
Con. Carbon Residue	0.02	0.56	0.98	
ASTM Ash	0.00	0.00	0.00	
Specific Dispersion	111.6	119	122.5	
Sulfur, Percent	0.16	0.33	0.09	

The additives and oil compositions of my invention were evaluated by a number of conventional and specially devised test methods including the following:

Copper strip activity (CRC L–16–445). —This procedure is used to determine the chemical activity toward copper. A copper strip one-half inch wide and three inches long is placed in a one-inch diameter test tube and covered with oil. The degree of discoloration of the copper strip as well as the temperature and duration of the test shall be recorded. The MIL–L–2105 specification requires no blackening after one hour at 250° F.

Rust protection (CRC L–13–445).—This test is intended to indicate the rust protective characteristics of universal gear lubricants.

A specially shaped SAE 1020 cold rolled steel paddle is rotated at 550 R. P. M. in a beaker containing 200 grams of the oil and 5 cc. of water at 180° F. After four hours on test, the paddle is rinsed in naphtha and inspected. Passing results must show no rust.

Modified almen (or Falex) rust test.—This test is currently an optional alternate for the CRC L–21–445 rust test. This test is intended to measure the rust protective characteristics of a thin film of gear lubricants on steel bearings which have been run under E. P. conditions at elevated temperature and stored under conditions of high relative humidity.

This modification employs the pin and bushings from a Falex test which has been run at a load of 500# for 25 minutes at a minimum oil temperature of 200° F. or higher depending on the frictional heat generated. The pin and bushings are placed in individual crucibles and drained for 30 minutes in an oven at a temperature of 180° F. Then they are placed under a bell jar approxi-

mately 10 inches in diameter along side a 250 cc. Griffin beaker containing about 100 cc. of tap water. This assembly is stored at a room temperature of approximately 75° F. for 24 hours. The test specimens are then cleaned with solvents and inspected for rust. A rating of ten indicates no rusting and zero indicates heavy rusting or staining.

Ratings of 8—9 are considered acceptable for MIL–L–2105 government specification universal gear Lubricants.

Timken L–20 weedout procedure #3.—A Timken machine is run 16 hours at 250° F., 200 R. P. M. and 198# lever load with the test block mounted on a special lever which reciprocates horizontally beneath the test cup a distance of 0.13 inch four times per minute. This arrangement produces an extremely high unit pressure at essentially line contact conditions. Therefore, unit pressures do not decrease appreciably as wear on the test block increases. The test is very useful in indicating the relative performance of lubricants in the costly CRC L–20 axle test or similar "Endurance" type tests.

A total wear on the test cup and block below about 50 mg. with no evidence of score or surface fatigue has been found to indicate lubricants which are passing or near passing in the CRC L–20 axle test. Commercial hypoid gear lubricants which pass the CRC L–20 axle test usually give from 20 to 50 mg. total wear on the cup and block and smooth fairly bright wear as in the L–20 axle, without evidence of surface fatigue. Typical S–Cl hypoid gear lubricants give up to 800 mg. wear and heavy ridging or score and indicate poor performance in "Endurance" or L–20 axle tests.

Gear oil procedure turbine oil rust test—GOP TORT procedure A.—A polished steel rod is immersed in a stirring mixture of 200 grams of gear lubricant and 5 grams of distilled water for 24 hours at 140° F. using the ASTM turbine oil rust test apparatus.

Commercially acceptable multi-purpose gear lubricants have been found to generally show no more than light rusting on the steel specimen either below or above the oil level. The test rod is washed in benzene at the completion of the test and air dried. Inspection is made under an Andrew technical service inspection light with a two power viewing lens. The areas above and below the oil level are rated separately as outlined below.

1. Definite rusting below the oil level is a failure.
2. Heavy rusting above the oil level is a failure.
3. Sludge or black precipitate in the used oil or beaker is generally cause for sample rejection.
4. Emulsification of the used oil is noted.

Sludge accumulation test—modified.—A 1-inch by 6-inch test tube containing 25 grams of oil and a 6-inch length of 0.04-inch diameter copper wire is blown with air at the rate of 0.5 liter per hour for 120 hours at a temperature of 250° F. At the end of 120 hours the ASTM naphtha insolubles in the oil and on the test tube are determined and recorded as the per cent sludge. The corrosion on the copper wire in mg. and any sludged or varnished appearance of the oil and test tube are recorded as a matter of information.

This test differs from the standard ASTM test in that the immersed copper wire catalyst is only about one-fourth as long as in the regular test and can be conveniently removed at any time to check the corrosion. Air is fed below instead of above the oil level because of the viscous nature of most gear oils and the slight aeration afforded by the regular ASTM D 670–42T procedure.

Uncompounded well refined mineral oils of 80–90 SUS viscosity at 210° F. show about 0.05 per cent sludge at 120 hours. Therefore, sludge values over about 0.1 per cent can usually be attributed to pro-sludging additives.

The total per cent of naphtha insolubles should generally not be more than about 0.1 per cent if reasonably stable 85+ V. I. oils are used unless pro-sludging additives are present. Pro-sludging additives may increase the insolubles to a substantial fraction of the additives present or as much as one or two per cent.

Test results on blends or phosphorized oils of the above examples are tabulated below:

TABLE II

TEST RESULTS ON BLENDS OF MINERAL OIL-PHOSPHORUS SULFIDE PREPARATIONS

Product of Example	1	2	3A	3B	4	5	6	Blank
Base Oil—Percent P_2S_5	B—7%	B—8.4%	B—14%	B—14%	D—Cyl. Stock—8.0%.	C—Penn—14%.	B—7%	Without Phosphorized Oil Product.
Base Oils, Weight Percent:								
A	35	35	36	36	38	35	35	33.
B	65	65	64	64	62	65	65	67.
Additives, Weight Percent:								
Phosphorized Oil	4.0	4.0	2.0	2.0	4.0	2.0	4.0	
Sulfurized Sperm Oil, 12% S	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5.
Chlorinated Paraffin, 42% Cl.	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5.
Lauric acid (rust inhibitor)	0.15	0.15				0.15	0.15	0.15.
Lauroyloxyacetic acid			0.15	0.15	0.15			
Acryloid 150	0.10	0.10	0.15	0.15	0.15	0.10	0.10	0.10.
DCF–200	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005.
Kin. Viscosity SUS @ 210° F.	85.7	85.22	84.9	84.8	84.8	84.2	84.1	84.9.
Cu Strip 1 hr. @ 250° F., CRC L–16–445.	Light Peacock.		Light Peacock.	Dark Peacock.	Dark Peacock.	Light Peacock.	Light Peacock.	Light Stain.
Inspection @ 30 days	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear.
Timken L–20 Proc. #3 Weedout Test:								
Wear, Cup and Block Total, mg.	25.1	21.5	20.3	13.7	20.3	18.6	19.4	484.
Burnish	Bright	Bright	Bright	Bright	Bright	Bright	Bright	
Score	None	None	None	None	Traces lines.	Traces lines.	Traces lines.	Heavily scored.
Sludge Accumulation at 120 hrs., Modified:								
Sludge, Percent	0.014	0.021	0.05	0.06	0.01	0.003	0.009	0.02.
Tube Deposits, Percent	0.005	0.009	0.02	0.05	0.00	0.002	0.000	0.00.
Rust Protection:								
Gear Oil Procedure Turbine Oil Rust Test A.	Perfect	Pass, Light gray.	Fail, Heavy black.	Light film rust.	Very light film rust.	Very light film rust.	Fail, Heavy black.[1]	None.
CRC L–13–445	Pass, light gray.	Pass, light gray.	Fail, rust and black.	Pass, light blue.		Pass, gray stain.	Fail, loose black.	Traces.
Falex Rust Test	9			9				

[1] Turns to a rust brown coat in 24 additional hours on test.

TABLE III

	Test Results on Blends of Example 1 (Base Oil "B"—7% P_2S_5)				Base Oil Blank
Base Oils, Weight Percent:					
A	26	38	30	30	24.
B	74	62	70	70	76.
Additives, Weight Percent:					
Phosphorized oil	1. 33	2. 0	4. 0	4. 0	
Sulfurized sperm oil, 12% S	1. 5	4. 5	4. 5	4. 5	
Chlorinated Paraffin, 42% Cl	1. 5	4. 5			
Chlorinated Naphthalene, 57% Cl			2. 0		
Lauric Acid (rust inhibitor)	0. 05				
Partially esterified alpha-hydroxy lauric acid		0. 05			
Acryloid 150	0. 10	0. 15	0. 10	0. 10	0. 10.
DCF-200	0. 005	0. 005	0. 005	0. 05	0. 05.
Lauroyloxyacetic acid		0. 10			
Kinematic Viscosity, SUS @ 210° F	87. 7	82. 14	86. 6	89. 8	89. 0
Cu Strip, 1 hr. @ 250° F., CRC L-16-445		Light Peacock	Dark Peacock	Dark Peacock	Perfect.
Timken L-20 Proc. #3 Weedout Test:					
Wear, Cup and Block Total, mg	7. 5	19. 5	18. 4	16. 7	
Burnish	Bright	Bright	Bright	Bright	
Score	None	Light lines	None	None	Very Hvy. score @ 30 mins.[1]
SAE Machine @ 1000 R. P. M., CRC 6-17-545			80#	89	37.
Sludge Accumulation @ 120 hrs., Modified:					
Sludge, Percent		0. 01	0. 032	0. 020	0. 00.
Tube Deposits, Percent		0. 00	0. 005	0. 004	0. 00.
Rust Protection:					
Gear Oil Proc. Turbine Oil Rust Test A		Light rust	Light gray stain.	Light blue stain.	Fail, 5% heavy rust.
CRC L-13-445				Gray blue stain.	Fail, 100% light rust.
Falex Rust Test			10 Perfect	10	

[1] Similar tests at lever loads of 75# give 9.2 mg. bright smooth wear and usually scores heavily at 100# lever load.

My invention provides a valuable means for imparting extreme pressure properties to mineral oils. Low cost, readily available materials are employed. Yields based on phosphorus pentasulfide, the most expensive ingredient, are improved and processing and equipment costs are minimized in contrast to previous comparable methods. The resulting products in conjunction with conventional sulfur and chlorine containing E. P. additives are characterized by capacity to meet the high speed (CRC L-19-645) and high torque (CRC L-20-545) axle tests which are intended to simulate opposite extremes of service and which are fundamental evaluation tests for MIL-L-2105 government specification universal gear lubricants. Pro-sludging, pro-corrosive and rusting components are minimized or eliminated and useful E. P. life is extended.

I claim:

1. A steam-treated, clear, oil compatible, unneutralized reaction product of a mineral oil bright stock and about 7 to 17 per cent phosphorus pentasulfide at about 400° to 500° F., from which insolubles have been separated at a temperature of about 150°–250° F. prior to steam-treatment.

2. A lubricating oil composition which consists essentially of a mineral oil base and sufficient to impart extreme pressure characteristics of a steam-treated, clear, oil compatible, unneutralized reaction product of a mineral oil bright stock and about 7 to 17 percent phosphorus pentasulfide at about 400° to 500° F., from which insolubles have been separated at a temperature of about 150°–250° F. prior to steam-treatment.

3. The method of manufacturing an unneutralized lubricating oil extreme pressure additive which comprises reacting a mineral oil bright stock with about 7 to 17% phosphorus pentasulfide at about 400° to 500° F. for about 10 to 20 hours, cooling the reaction mixture to about 150° to 250° F., separating insolubles and blowing the mixture with steam until only traces of hydrogen sulfide evolve.

4. A clear, oil compatible, unneutralized organic phosphorus and sulfur containing composition which is the product prepared by reacting a mineral oil bright stock and about 7 to 17 per cent phosphorus pentasulfide at about 400° to 500° F. for about 10 to 20 hours, cooling the reaction mixture to about 150° to 250° F., separating insolubles and blowing the mixture with steam until only traces of hydrogen sulfide evolve.

5. A lubricating composition which consists essentially of a mineral oil base and 1 to 6 per cent of the unneutralized product prepared by reacting a mineral oil bright stock and about 7 to 17 per cent phosphorus pentasulfide at about 400° to 500° F. for about 10 to 20 hours, cooling the reaction mixture to about 150° to 250° F., separating insolubles and blowing the mixture with steam until only traces of hydrogen sulfide evolve.

6. A gear lubricating oil composition which consists essentially of a mineral oil base containing an extreme pressure additive selected from the group consisting of chlorinated wax, chlorinated naphthalene, sulfurized sperm oil and sulfurized lard oil, and 1 to 6 per cent of the unneutralized product prepared by reacting a mineral oil bright stock and about 7 to 17 per cent phosphorus penta-sulfide at about 400° to 500° F. for about 10 to 20 hours, cooling the reaction mixture to about 150° to 250° F., separating insolubles and blowing the mixture with steam until only traces of hydrogen sulfide evolve.

7. A clear, oil compatible, unneutralized organic phosphorous and sulfur containing composition which is the product prepared by reacting a mineral oil bright stock and about 7 to 17 per cent phosphorous pentasulfide at about 400° to 500° F. for about 10 to 20 hours, separating insolubles at an elevated temperature and blowing the mixture with steam until only traces of hydrogen sulfide evolve.

8. A lubricating composition which consists essentially of a mineral oil base and 1 to 6 per cent of the unneutralized product prepared by reacting a mineral oil bright stock and about 7 to 17 per cent phosphorous pentasulfide at about 400° to 500° F. for about 10 to 20 hours, separating insolubles at an elevated temperature and blowing the mixture with steam until only traces of hydrogen sulfide evolve.

9. The method of manufacturing an unneutralized lubricating oil extreme pressure additive which comprises reacting a mineral oil bright stock and about 7 to 17 per cent phosphorous pentasulfide at about 400° to 500° F. for about 10 to 20 hours, separating insolubles at an elevated temperature and blowing the mixture with steam until only traces of hydrogen sulfide evolve.

10. A gear lubricating oil composition which consists essentially of a mineral oil base containing an extreme pressure additive selected from the group consisting of chlorinated wax, chlorinated naphthalene, sulfurized

sperm oil and sulfurized lard oil, and 1 to 6 per cent of the unneutralized product prepared by reacting a mineral oil bright stock and about 7 to 17 per cent phosphorous pentasulfide at about 400° to 500° F. for about 10 to 20 hours, separating insolubles at an elevated temperature and blowing the mixture with steam until only traces of hydrogen sulfide evolve.

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