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LUBRICANT

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This invention relates to a lubricating oil composition characterized by improved properties with respect to oxidation and corrosion repression.

In my co-pending application, Serial No. 74,257, filed concurrently herewith, I have described and claimed new compositions of matter resulting from the reaction of a sulfur chloride with the reaction product of a bicyclic terpene, a phosphorus sulfide, and an alkylated phenol or an alcohol. I have discovered that the compounds to which this application is directed are especially effective in restraining the deterioration of lubricating oil compositions and the corrosion of metal parts in contact therewith. In particular, my novel lubricants exhibit a marked ability to promote engine cleanliness by inhibiting ring sticking, piston skirt varnish formation, deposition of sludge, and the like, as well as possessing favorable extreme pressure properties.

The proportions of the addends used in the compounding of my improved lubricating oil compositions may be varied somewhat but, in any case, only a minor proportion is used. The optimum proportion to be used will depend upon the particular use to which the lubricating oil composition is to be put, as well as being dependent upon the particular additive employed. Generally, the compounds should be used in a range of concentrations from 0.1% to about 10% as based upon the weight of the lubricating oil base constituent. In particular, I prefer and recommend an additive cencentration of about 0.5 to 2.5%.

The lubricating oil base constituent to be used may vary greatly, depending upon the intended use of the lubricant. Various petroleum lubricating oil fractions of special merit are, for instance, solvent-treated Mid-Continent neutrals or a blend of such Mid-Continent neutrals with bright stock or a solvent-refined lubricating oil fraction from a Pennsylvania crude.

Small quantities of various agents may be used in conjunction with these compounds without material effect upon the lubricating oil composition. Exemplary are detergents, for instance, a barium mahogany sulfonate, pour depressants, for instance, octadecyl methacrylate polymers, and foam inhibitors, such as silicone polymers.

The invention will be illustrated hereinafter by specific examples of my improved lubricating oil composition. However, since the characteristics of the lubricants are somewhat affected by the characteristics of the reaction product used in its compounding, the illustrations of my lubricants will include an initial description of the preparation, and examples, of various addends. Generally, these compounds are prepared by reacting initially a bicyclic terpene, for example, alpha-pinene, with a phosphorus sulfide, for example, phosphorus pentasulfide. This condensation product is then further reacted with an alkylated phenol or alcohol, and the resulting mixture is treated with a sulfur chloride. A bicyclic terpene, such as alpha-pinene or camphene, is employed in the formation of the intermediate condensation products, since the monocyclic terpenes result in the production of oil-insoluble compositions.

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In the preparation of the exemplary intermediate condensation product of, for example, alpha-pinene and phosphorus pentasulfide, the molar ratio of alpha-pinene to phosphorus pentasulfide employed with advantage is about 3:1. However, this ratio may vary somewhat in either direction. For instance, highly desirable condensation products result when the molar ratio of alpha-pinene to phosphorus pentasulfide is within the range of 5:2 to about 9:2.

The reaction of alpha-pinene with phosphorus pentasulfide is highly exothermic and proceeds spontaneously after being initiated by slight heating. A desirable method of effecting the reaction is to heat the alpha-pinene in a vessel to about 275° F., or slightly higher, and then, without further heating, slowly add the phosphorus pentasulfide in powdered form while maintaining agitation. The heat of the reaction is considerable, and consequently, the addition should be made slowly so as to avoid the possibility of the reaction becoming uncontrollable. In particular, a useful condensation product is prepared when the temperature during the admixture is not permitted to exceed about 275° F., although higher temperatures are permissible.

After the addition is completed, it is usually necessary to apply heat externally to complete the reaction. The temperature during this latter stage is preferably maintained at about 275° F., although thermal environments in the range of about 200–400° F. may be employed. The condensation product prepared in this manner is a viscous liquid at elevated temperatures, and solidifies upon cooling to room temperature.

To this mixture is gradually added an alkylated phenol or alcohol, advantageously at a temperature of about 275° F. The optimum temperature of the condensation product for the introduction of the phenol or alcohol will vary, depending upon the phenol or alcohol used. In particular, alkylated phenols are relatively stable towards heat, and they may be safely admixed with the condensation product at temperatures

as high as 300° F. Very little heat is evolved upon the addition of the phenol, and after its addition the mixture is preferably maintained at an elevated temperature for a short period of time, although this is not necessary. The proportions of the alkylated phenol or alcohol to be added may be varied over a considerable range, depending upon the particular characteristics of the product desired. The optimum proportion of the phenol or alcohol used is, to a considerable extent, dependent upon the ratio of alpha-pinene to phosphorus pentasulfide used in the preparation of the condensation product. Generally satisfactory results have been obtained employing an alkylated phenol or alcohol in the ratio of 0.5:2 to 3.0:2, based on the molar quantities of the phosphorus pentasulfide.

Due to the viscosity of this reaction product, it is highly preferable to add at this point a light neutral oil for ease of handling. In practice, the neutral oil addition should be of such an amount as to yield an oil concentrate containing about 3% phosphorus. Other inert solvents, e. g., chloroform or carbon tetrachloride, could of course be used, but an oil is favored for cost and because the products are generally most useful in the form of oil concentrates.

The final step in the production of these compositions is the addition of a sulfur chloride, preferably effected at a temperature of the reaction product (advantageously prepared as an oil concentrate) in the range of 100 to 120° F. This addition temperature of the sulfur chloride is dependent in part upon the particular chloride used. In particular, where the lower-boiling dichloride is employed, the temperature is advantageously maintained within these limits. Excessive temperatures also result in discoloration of the preparation and should be avoided for this reason. Accordingly, the sulfur chloride is added slowly to keep the temperature below about 120° F., and upon completion of the addition, the composition thus prepared may be further reacted at a temperature of about 200° F. for five to ten hours. However, in order to render preparation of these compositions more practicable, this final reaction period may be eliminated.

The proportions of the sulfur chloride employed may be varied over a wide range, depending upon the properties of the finished composition desired as well as upon the type of sulfur chloride added. Based upon the amount of phosphorus pentasulfide utilized, the addition of the sulfur chloride may be preferably in the range of 0.5:2 to 5.0:2.

A particularly satisfactory range of proportions of constituents to be used in preparing these compositions consists of reacting about 8 moles of alpha-pinene to about 2 moles of phosphorus pentasulfide to about 0.5 to 2.0 moles of an alkylated phenol or alcohol to about 0.5 to 5.0 moles of sulfur chloride.

The composition thus prepared is generally acidic and neutralization treatment may be employed in order to eliminate the absorbed hydrogen chloride and the labile chloride present. A particularly satisfactory neutralization treatment comprises heating these compositions to 200° F. for a period of about thirty to forty-five minutes, whereupon 1½ moles of calcium hydroxide are added for each mole of the sulfur chloride employed. This mixture is then heated for three hours at 200° F. while maintaining vigorous agitation. The finely suspended calcium compounds in the neutralized composition may be removed upon the addition of a filter aid and a subsequent filtration. However, other alkaline earth oxides and hydroxides, such as calcium oxide, barium oxide, and barium hydroxide, may be used. The optimum quantities of the neutralizing agent employed are dependent upon the acidic properties of the reaction product initially prepared.

Pure alpha-pinene is preferred in preparing these compositions; however, a reactant comprising substantially alpha-pinene in admixture with other related terpenes, such as camphenes and dipentenes, is satisfactory.

Exemplary of alkylated phenols that may be used are para-tertiary amyl phenol, para-cyclohexyl phenol, di-tertiary amyl phenol, and di-secondary amyl phenol. As indicated above, an alcohol may be used to replace all or part of the alkylated phenol in the compound, examples of which are 2-methyl pentanol, 2-ethyl butanol, and octanol-1. The alcohols are favored by cost considerations and in part by the circumstance that the relatively pleasing odor of some higher alcohols acts to some extent as a masking odor. In general, however, the phenol-containing products are found to be superior.

The sulfur chloride employed may be either the monochloride or the dichloride. However, sulfur dichloride is recommended and preferred because, inter alia, the absorbed hydrogen chloride and labile chlorine are more easily removed, thereby requiring a milder neutralization treatment.

The following specific examples of various members, and the procedure by which they can be successfully prepared, including neutralization treatments, are given as illustrative of this group of compounds. The light petroleum lubricating oil fraction used as the diluent in the examples was a Mid-Continent conventionally-refined neutral having the characteristics set forth in Table I.

TABLE I

Gravity °A. P. I.	27–28
Flash point, °F.	355–360
Fire point, °F.	410
S. U. S. viscosity at:	
100° F., secs.	105
130° F., secs.	65
210° F., secs.	39
Viscosity index	60–65
Color	2—
Pour point, °F.	+15
Carbon, residue, per cent	.01
Acid number	.01
Sulfur, per cent	.50
Aniline number	83
Specific dispersion	132

EXAMPLE I

544 gms. (4 moles) of alpha-pinene were added to a five-liter, three-necked flask equipped with a reflux condenser, stirrer, and thermometer. The alpha-pinene was heated to 275° F., whereupon 222 gms. (1 mole) of phosphorus pentasulfide were slowly added portionwise so as to maintain the temperature at 275° F. Upon completion of the addition, the mixture was heated for seven hours at 275° F., and then 164 gms. (1 mole) of para-tertiary amyl phenol were added and the resulting mixture heated for four hours at 275° F. The product was diluted with 1035 gms. of neutral oil so as to yield an oil concentrate containing an equivalent of, by weight,

11.3% phosphorus pentasulfide. The temperature was lowered to 100° F., and 11 gms. (0.1 mole) of sulfur dichloride were slowly added from a dropping funnel at a rate so as to maintain the temperature between 100 and 110° F. The addition of the sulfur dichloride required two hours. 10 gms. (0.18 mole) of calcium oxide were then contacted with the mixture for 0.5 hour at a temperature of 200° F., whereupon 2% filter aid was added and the mixture filtered. The finished product was slightly basic and analyzed by weight 0.2% chlorine, 3.28% phosphorus, 8.60% sulfur, and 0.018% calcium. However, this compound still had a garlic odor.

EXAMPLES II–X

544 gms. (4 moles) of alpha-pinene were added to a five-liter, three-necked flask, equipped with a reflux condenser, stirrer, and thermometer. The alpha-pinene was heated to 275° F., whereupon 222 gms. (1 mole) of phosphorus pentasulfide were slowly added portionwise so as to maintain the temperature at 275° F. Upon completion of the addition, the mixture was heated for seven hours at 275° F. and then 164 gms. (1 mole) of para-tertiary amyl phenol were added and the resulting mixture heated for four hours at 275° F. The product was diluted with 1035 gms. of neutral oil so as to yield an oil concentrate containing an equivalent of, by weight, 11.3% phosphorus pentasulfide. The temperature was lowered to 100° F. and 52 gms. (0.5 mole) of sulfur dichloride were slowly added from a dropping funnel at a rate so as to maintain the temperature between 100 and 115° F. The addition of the sulfur chloride required three hours.

Convenient amounts, about one third of a compound prepared in this manner, were then contacted with various neutralizing agents for different periods of time and at different temperatures. In each case 2% filter aid was added to the neutralized preparation and the mixture filtered. The individual treatments and the analyses of the different products thereby formed follow. Where there was an absence of acidity, each compound was found to be slightly basic, which is indicated as "S. B." in the examples.

EXAMPLE XI

544 gms. (4 moles) of alpha-pinene were added to a five-liter, three-necked flask equipped with a reflux condenser, stirrer, and thermometer. The alpha-pinene was heated to 275° F. and 222 gms. (1 mole) of phosphorus pentasulfide were slowly added portionwise so as to maintain the temperature at 275° F. Upon completion of the addition, the mixture was heated for seven hours at 275° F., whereupon 164 gms. (1 mole) para-tertiary amyl phenol were added and the resulting mixture heated for four hours at 275° F. The product was then diluted with 1035 gms. of neutral oil so as to yield an oil concentrate containing an equivalent of, by weight, 11.3% phosphorus pentasulfide. The temperature was lowered to 100° F. and 77 gms. (0.75 mole) of sulfur dichloride were added over a period of four hours at such a rate as to maintain a temperature between 100 and 115° F. This compound was reacted for an additional five hours at 200° F. 35 gms. (0.62 mole) of calcium oxide were then added and contacted therewith for 0.5 hour at 200° F., whereupon 2% filter aid was added and the mixture filtered. The finished product analyzed by weight 0.05% acidity as hydrogen chloride, 0.95% chlorine, 3.20% phosphorus, 9.78% sulfur, and 0.003% calcium, and possessed a pine odor.

EXAMPLE XII

680 gms. (5 moles) of alpha-pinene were added to a five-liter, three-necked flask equipped with a reflux condenser, stirrer, and thermometer. The alpha-pinene was heated to 275° F. and 222 gms. (1 mole) of phosphorus pentasulfide were slowly added portionwise so as to maintain the temperature at 275° F. Upon completion of the addition, the mixture was heated for seven hours at 275° F., whereupon 164 gms. (1 mole) of para-tertiary amyl phenol were added and the resulting mixture heated for four hours at 275° F. The product was then diluted with 899 gms. of the neutral oil so as to yield an oil concentrate containing an equivalent of, by weight, 11.3% phosphorus pentasulfide. The temperature was then lowered to 100° F. and 258 gms. (2.5 moles) of sulfur dichloride were slowly added from a drop-

Example	II	III	IV	V	VI
Neutralization Agent	CaO	CaO	CaO	$Ca(OH)_2$	$Ca(OH)_2$
Grams	10	20	28	20	20
Moles	0.18	0.36	0.5	0.27	0.27
Time, hrs	3.5	5.0	5.0	1.0	2.0
Temperature, ° F	250	250	200	200	200
Acidity as Hydrogen Chloride, Wt. Percent	0.06	S. B.	S. B.	0.003	S. B.
Chlorine, Wt. Percent	0.52	0.2	0.5	0.55	0.44
Phosphorus, Wt. Percent	3.08	3.24	3.28	2.64	2.64
Sulfur, Wt. Percent	9.29	9.29	9.30	9.28	9.25
Calcium, Wt. Percent	0.52	0.164	0.030	0.002	0.002
Odor	Pine	Pine	Pine	Pine	Pine

Example	VII	VIII	IX	X
Neutralization Agent	$Ca(OH)_2$	$Ba(OH)_2.8H_2O$	BaO	CaO
Grams	20	53	26	10
Moles	0.27	0.17	0.17	0.18
Time, hrs	3.0	3.0	3.0	3.0
Temperature, ° F	200	200	200	200
Acidity as Hydrogen Chloride, Wt. Percent	0.009	0.03	0.05	0.03
Chlorine, Wt. Percent	0.67	0.31	0.066	0.40
Phosphorus, Wt. Percent	2.72	2.76	2.74	2.78
Sulphur, Wt. Percent	9.19	8.58	4.33	9.26
Calcium, Wt. Percent	0.002			0.004
Barium, Wt. Percent		0.843	0.060	
Odor	Pine	Pine	Pine	Pine

ping funnel at a rate so as to maintain the temperature between 100 and 120° F. The addition of the sulfur dichloride required eight hours, whereupon the temperature was increased to 200° F. and so maintained for five hours. 100 gms. (1.8 moles) of calcium oxide were then contacted with the mixture for 0.5 hour at a temperature of 200° F., whereupon 2% filter aid was added and the mixture filtered. The finished product analyzed by weight 0.07% acidity as hydrogen chloride, 2.80% chlorine, 3.26% phosphorus, 11.66% sulfur, and 0.03% calcium, and possessed a camphor odor. As the treatment time was short, free hydrogen chloride developed in the product and it was necessary to retreat it.

This product was retreated by addition of 100 gms. (1.8 moles) of calcium oxide. The treatment lasted for four hours at a temperature of 200° F. The reneutralized composition then analyzed by weight 0.04% acidity as hydrogen chloride, 2.54% chlorine, 3.26% phosphorus, 11.92% sulfur, and 0.00% calcium, and possessed a camphor odor.

EXAMPLES XIII–XV

544 gms. (4 moles) of alpha-pinene were added to a five-liter, three-necked flask, equipped with a reflux condenser, stirrer, and thermometer. The alpha-pinene was heated to 275° F., whereupon 22 gms. (1 mole) of phosphorus pentasulfide were slowly added portionwise so as to maintain the temperature at 275° F. Upon completion of the addition, the mixture was heated for seven hours at 275° F. 164 gms. (1 mole) of para-tertiary amyl phenol were then added and the resulting mixture heated for four hours at 275° F. The product was diluted with 1035 gms. of the neutral oil so as to yield an oil concentrate containing an equivalent of, by weight, 11.3% phosphorus pentasulfide. The temperature was then lowered to 100° F. and 31 gms. (0.3 mole) of sulfur dichloride were slowly added from a dropping funnel at a rate so as to maintain the temperature between 100 and 110° F.

Convenient amounts, about one third of a compound prepared in this manner, were then contacted with various amounts of calcium oxide and calcium hydroxide for three hours at 200° F. In each case 2% filter aid was added to the neutralized preparation and the mixture filtered. The individual neutralization agents employed and the analyses of the different products thus formed follow. Where there was an absence of acidity, each compound was found to be slightly basic, which is indicated as "S. B." in the examples.

Example	XIII	XIV	XV
Neutralization Agent	CaO	CaO	$Ca(OH)_2$
Grams	6	11	15
Moles	0.1	0.2	0.2
Acidity as Hydrogen Chloride, Wt. Percent	S. B.	S. B.	0.10
Chlorine, Wt. Percent	0.3	0.5	1.20
Phosphorus, Wt. Percent	3.36	3.38	2.98
Sulfur, Wt. Percent	8.86	9.00	8.99
Calcium, Wt. Percent	0.003	0.32	0.00
Odor	Pine	Pine	Pine

EXAMPLE XVI

1088 gms. (8 moles) of alpha-pinene were added to a five-liter, three-necked flask, equipped with a reflux condenser, stirrer, and thermometer. The alpha-pinene was heated to 275° F., whereupon 444 gms. (2 moles) of phosphorus pentasulfide were slowly added portionwise so as to maintain the temperature at 275° F. Upon completion of the addition, the mixture was heated for seven hours at 275° F., following which 256 gms. (1.56 moles) of para-tertiary amyl phenol were added and the resulting mixture heated for four hours at 275° F. Following the addition of the phenol, 19 gms. (0.19 mole) of 2-methyl pentanol were further added and the entire mixture heated for four additional hours at 275° F. The product was diluted with 2123 gms. of the neutral oil so as to yield an oil concentrate containing an equivalent of, by weight, 11.3% phosphorus pentasulfide. The temperature was lowered to 100° F. and 103 gms. (1 mole) of sulfur dichloride were slowly added from a dropping funnel at a rate so as to maintain the temperature between 100 and 120° F. The addition of the sulfur chloride required about three hours. 111 gms. (1.5 moles) of calcium hydroxide were then added, and contacted therewith for three hours at 200° F. 2% filter aid was added and the mixture filtered. The compound was slightly basic and analyzed by weight .62% chlorine, 3.14% phosphorus, 9.10% sulfur, and 0.00% calcium, had an acid number of 1.20 and an alcoholic-pine odor.

EXAMPLE XVII

1088 gms. (8 moles) of alpha-pinene were added to a five-liter, three-necked flask, equipped with a reflux condenser, stirrer, and thermometer. The alpha-pinene was heated to 275° F., whereupon 444 gms. (2 moles) of phosphorus pentasulfide were slowly added portionwise so as to maintain the temperature at 275° F. Upon completion of the addition, the mixture was heated for seven hours at 275° F. and then 256 gms. (1.56 moles) of para-tertiary amyl phenol were added and the resulting mixture heated for four hours at 275° F. The product was diluted with 2140 gms. of neutral oil so as to yield an oil concentrate containing an equivalent of, by weight, 11.3% phosphorus pentasulfide. The temperature was lowered to 100° F., and 103 gms. (1 mole) of sulfur dichloride were slowly added from a dropping funnel at a rate so as to maintain the temperature between 100 and 120° F. The addition of the sulfur chloride required about three hours. 111 gms. (1.5 moles) of calcium hydroxide were then added and contacted therewith for three hours at 200° F. 2% filter aid was added and the mixture filtered. The compound was slightly basic and analyzed by weight 0.5% chlorine, 3.18% phosphorus, 9.04% sulfur, and 0.00% calcium, had an acid number of 0.95 and possessed a pine odor.

EXAMPLE XVIII

544 gms. (4 moles) of alpha-pinene were added to a five-liter, three-necked flask, equipped with a reflux condenser, stirrer, and thermometer. The alpha-pinene was heated to 275° F., whereupon 222 gms. (1 mole) of phosphorus pentasulfide were slowly added portionwise so as to maintain the temperature at 275° F. Upon completion of the addition, the mixture was heated for seven hours at 275° F. and 164 gms. (1 mole) of para-tertiary amyl phenol were added, the resulting mixture being heated for four hours at 275° F. The product was diluted with 1035 gms. of neutral oil so as to yield an oil concentrate containing an equivalent of, by weight, 11.3% phosphorus pentasulfide. The temperature was lowered to 100° F. and 68 gms. (0.5 mole) of sulfur monochloride were slowly added from a dropping funnel at a rate so as to maintain the

temperature between 100 and 115° F. The addition of the sulfur monochloride required about three hours. 37 gms. (0.5 mole) of calcium hydroxide were then added. After contacting for three hours at 200° F., 2% filter aid was added and the mixture filtered. This compound contained an appreciable amount of hydrogen chloride and hence retreatment was necessary. Accordingly, the treated product was divided into two parts. To one part were added 19 gms. (0.25 mole) of calcium hydroxide and contacted therewith for three hours at 200° F. This composition analyzed by weight 0.07% acidity as hydrogen chloride, 0.87% chlorine, 3.40% phosphorus, and 9.85% sulfur, and possessed a pine odor. The remaining one half was treated in an identical manner except that the contact temperature was 250° F. This composition was slightly basic and analyzed by weight 0.43% chlorine, 3.54% phosphorus, 9.92% sulfur, and 0.124% calcium, and also possessed a pine odor.

For the purpose of further illustrating my invention, I have compounded various lubricating oil compositions containing certain addends. In particular, compositions B and C, which follow, identify lubricants within the scope of my invention. In the exemplary compositions, the sulfonated mineral oil addend employed was a 10% concentrate of barium mahogany sulfonate in mineral oil. The pour depressant was a polymer of octadecyl methacrylate in a hydrocarbon base, while the foam inhibitor was a silicone polymer. Although the various additives, such as these three, may be compounded into the lubricating oil compositions, the practice of my invention does not necessarily contemplate the use of such constituents.

Composition A

The lubricating oil composition was composed substantially of by weight:

	Per cent
Solvent-treated Mid-Continent neutral oil	100
Foam inhibitor	0.0005

The properties of this lubricant were found to be:

Gravity, °A. P. I.	30.4
Flash point, °F.	400
Fire point, °F.	455
S. U. S. viscosity at:	
100° F. secs.	154
130° F. secs.	85
210° F. secs.	43.1
Pour point, °F.	15
Color, N. P. A.	2
Carbon Residue, wt. per cent	0.01
Acid number	0.00
Barium, wt. per cent	None
Phosphorus, wt. per cent	None

The lubricating oil composition was tested in a Chevrolet engine by the CRC L–4–545 procedure (Ordnance Department specification AXS 1554). The varnish and sludge ratings, both individual and total, were found to be:

Varnish ratings

Piston skirts	2.0
Rocker arm cover plate	8.0
Push rod cover plate	9.0
Cylinder walls	2.5
Crankcase oil pan	1.5
Total	23.0

Sludge ratings

Rocker arm assembly	2.0
Rocker arm cover plate	4.0
Push rod cover plate	5.5
Oil screen	7.5
Crankcase oil pan	5.5
Total	24.5

The total varnish and sludge rating was 47.5. The bearing loss was 0.718 gm. per whole bearing, while 0.097 quart of oil was consumed per hour. A test of the used oil after 36 hours indicated a 136% viscosity rise at 100° F. The acid and saponification numbers were 7.3 and 30.4, respectively.

This lubricant did not include the novel addends I have described hereinbefore.

Composition B

The lubricating oil composition was composed substantially of by weight:

	Per cent
Solvent-treated Mid-Continent neutral oil	98.5
Compound of Example XVI	1.5
Foam inhibitor	0.0005

The properties of this lubricant were found to be:

Gravity, °A. P. I.	29.3
Flash point, °F.	400
Fire point, °F.	455
S. U. S. viscosity at:	
100° F., secs.	164.1
130° F., secs.	90.2
210° F., secs.	44.0
Pour point, °F.	10
Color, N. P. A.	2½—
Carbon residue, wt. per cent	0.13
Acid Number	0.08
Barium, wt. per cent	None
Phosphorus, wt. per cent	0.046

The lubricating oil composition was tested in a Chevrolet engine by the CRC L–4–545 procedure (Ordnance Department specification AXS 1554). The varnish and sludge ratings, both individual and total, were found to be:

Varnish ratings

Piston skirts	5.5
Rocker arm cover plate	10.0
Push rod cover plate	10.0
Cylinder walls	6.0
Crankcase oil pan	9.0
Total	40.5

Sludge ratings

Rocker arm assembly	9.0
Rocker arm cover plate	9.0
Push rod cover plate	8.5
Oil screen	9.0
Crankcase oil pan	9.0
Total	44.5

The total varnish and sludge rating was 85.0. The bearing loss was 0.025 gm. per whole bearing, while 0.067 quart of oil was consumed per hour. A test of the used oil after 36 hours indicated a 23.7% viscosity rise at 100 F. The acid and saponification numbers were 0.55 and 6.18, respectively.

The test on this used lubricating composition, which is encompassed by my invention, revealed a reduced oxidation as evidenced by a lower

acid number, saponification number, and viscosity rise.

Composition C

The lubricating oil composition was composed substantially of by weight:

	Per cent
Solvent-treated Mid-Continent neutral oil	88.4
Sulfonated mineral oil	10.0
Compound of Example XVI	1.5
Pour depressant	0.1
Foam inhibitor	0.0005

The properties of this lubricant were found to be:

Gravity, °A. P. I.	29.7
Flash point, °F.	400
Fire point, °F.	450
S. U. S. viscosity at:	
100° F., secs.	167.2
130° F., secs.	91.2
210° F., secs.	44.5
Pour point, °F.	−15
Color, N. P. A.	3½−
Carbon residue, wt. per cent	0.70
Acid number (Basic)	0.53
Barium, wt. per cent	0.360
Phosphorus, wt. per cent	0.045

The lubricating oil composition was tested in a Chevrolet engine by the CRC L-4-545 procedure (Ordnance Department specification AXS 1554). The varnish and slude ratings, both individual and total, were found to be:

Varnish ratings

Piston skirts	9.5
Rocker arm cover plate	10.0
Push rod cover plate	10.0
Cylinder walls	9.5
Crankcase oil pan	10.0
Total	49.0

Sludge ratings

Rocker arm assembly	9.5
Rocker arm cover plate	9.5
Push rod cover plate	9.0
Oil screen	10.0
Crankcase oil pan	9.0
Total	47.0

The total varnish and sludge rating was 96.0. The bearing loss was 0.089 gm. per whole bearing, while 0.036 quart of oil was consumed per hour. A test of the used oil after 36 hours indicated a 25% viscosity rise at 100° F. The acid and saponification numbers were 1.60 and 9.7, respectively.

The test on this used lubricating composition which is encompassed by my invention, revealed reduced oxidation as evidenced by a lower acid number, saponification number, and viscosity rise. In addition, the test indicates that the novel additives may be used conjunctively with other addends.

I claim:

1. A lubricating oil composition comprising predominantly a mineral oil and containing about 0.1 to 10 per cent of a compound prepared by the reaction at about 100° to 200° F. of about 0.5 to 5.0 moles of a sulfur chloride with the reaction product prepared at about 250° to 400° F. of about 5 to 9 moles of a bicyclic terpene, about 2 moles of a phosphorus sulfide, and about 0.5 to 3.0 moles of a compound selected from the class consisting of lower alkylated monohydric phenols and lower aliphatic monohydric alcohols.

2. A lubricating oil composition comprising predominantly a mineral oil and containing about 0.1 to 10 per cent of a compound prepared by the reaction at about 100° to 200° F. of about 0.5 to 5.0 moles of a sulfur chloride with the reaction product prepared at about 250° to 400° F. of about 5 to 9 moles of alpha-pinene, about 2 moles of phosphorus pentasulfide, and about 0.5 to 3.0 moles of a lower alkylated monohydric phenol.

3. A lubricating oil composition comprising predominantly a mineral oil and containing about 0.1 to 10 per cent of a compound prepared by the reaction at about 100° to 200° F. of about 0.5 to 5.0 moles of a sulfur chloride with the reaction product prepared at about 250° to 400° F. of about 5 to 9 moles of alpha-pinene, about 2 moles of phosphorus pentasulfide, and about 0.5 to 3.0 moles of a lower aliphatic monohydric alcohol.

4. A lubricating oil composition comprising predominantly a mineral oil and containing about 0.1 to 10 per cent of a compound prepared by the addition at 100° to 120° F. of about 0.5 to 5.0 moles of sulfur dichloride and reaction at about 100° to 200° F. with the reaction product prepared at about 250° to 400° F. of about 5 to 9 moles of alpha-pinene, about 2 moles of phosphorus pentasulfide, and about 0.5 to 3.0 moles of a compound selected from the class consisting of lower alkylated monohydric phenols and lower aliphatic monohydric alcohols.

5. A lubricating oil composition comprising predominantly a mineral oil and containing about 0.1 to 10 per cent of a compound prepared by the addition at 100° to 120° F. of about 0.5 to 5.0 moles of a sulfur chloride and reaction at about 100° to 200° F. with the reaction product prepared at about 250° to 400° F. of about 5 to 9 moles of alpha-pinene, about 2 moles of phosphorus pentasulfide, and about 0.5 to 3.0 moles of a compound selected from the class consisting of lower alkylated monohydric phenols and lower aliphatic monohydric alcohols.

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