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2,939,841

## HIGH V.I. DETERGENT LUBRICATING OILS

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This invention relates to high V.I. detergent mineral lubricating oils, to addition agents capable of imparting such characteristics to mineral lubricating oils, and to methods of preparing said addition agents and lubricating oils. More particularly the invention relates to oil-soluble metal salts of acidic, phosphorus-containing reaction products obtained by reacting under oxidizing conditions high molecular weight olefin polymers or olefin-diolefin copolymers with phosphorus trichloride with or without subsequent treatment with a phosphorus sulfide and to lubricating oils containing such oil-soluble metal salts.

Internal combustion engines, both of the spark-ignition and compression-ignition types, are constantly being modified to give among other improvements increased efficiency and greater horsepower output. With these changes, improvements in lubricating oils suitable for use in these engines are necessary.

One of the important characteristics of a lubricating oil, if it is to operate efficiently in such engines, is that it does not change greatly in viscosity with change in temperature. This viscosity-temperature relationship is measured or denoted by viscosity index (V.I.), a high V.I. oil being one that has a relatively small change in viscosity with changes in temperature. The use of various polymeric materials to improve the V.I. of lubricating oils is known, however the polymers which have been used have a tendency to break down in use probably because of the shearing effect in bearings, gears and the like so that the V.I. of an oil containing these materials tends to decrease when the oil is used for appreciable periods of time.

Moreover, the polymers have a tendency to deposit on heated engine parts such as the stems and tulips of intake valves where the amount of oil supplied to such parts is relatively small.

Another important characteristic of a lubricating oil which is to be used in internal combustion engines is that of detergency, i.e., the ability of the oil to prevent the formation of carbon and/or varnish-like deposits in the engine, particularly on pistons and cylinder walls, in ring grooves, in hydraulic valve lifters, and the like.

Still another characteristic of a lubricating oil suitable for use in the described engines is that it is capable of preventing the formation of and/or the build-up of acidic bodies in the oil during use, thus greatly reducing or preventing the corrosion of metal parts in the engine.

It is an object of this invention to provide a lubricating oil having the characteristics of high viscosity index and high detergency.

It is another object of this invention to provide a lubricating oil suitable for use in internal combustion engines, which oil has a high viscosity index which does not decrease appreciably during use and which prevents the formation of carbon and/or varnish-like deposits in the engine.

A further object of this invention is to provide a lubricating oil having the characteristics described which

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consists of a lubricating oil containing a single additive material which is effective in imparting all of these characteristics.

Still another object of this invention is to provide a composition suitable for addition to mineral lubricating oil and which has the effect of imparting high V.I. and detergency characteristics to said oil.

Still another object of the invention is to provide a method for the preparation of an additive composition adapted for addition to mineral lubricating oil to impart the high V.I. and detergency characteristics to said oil.

The invention resides in compositions of matter adapted for addition to mineral lubricating oil and in the method of preparing these compositions. The compositions comprise an oil-soluble metal salt of the acidic reaction product obtained by reacting an aliphatic hydrocarbon polymeric material having a molecular weight generally above 5000 and preferably above 10,000 and generally below about 200,000, preferably below about 100,000, which may be an olefin polymer or an olefin-diolefin copolymer with phosphorus trichloride while bubbling gaseous oxygen through the reaction mixture at a temperature between about 10° C. and about 100° C. The invention resides also in lubricating oils containing sufficient of the described oil-soluble metal salt to impart high V.I. and high detergency characteristics to said oil.

The invention resides also in oil-soluble metal salts of reaction products obtained by first treating the polymeric material with phosphorus trichloride in the presence of gaseous oxygen and subsequently reacting that product with 2 to 10% by weight based on the polymeric material of a phosphorus sulfide such as phosphorus pentasulfide at a temperature between about 150° C. and about 200° C. It resides also in lubricating oils containing oil-soluble metal salts of this latter reaction product.

The invention resides further in oil-soluble metal salts of the types described which are further reacted with excess metal base to impart alkaline reserve to lubricating oils containing such additives.

In preparing lubricating oil addition agents according to this invention, a polyolefin, as for example a polybutene of approximately 30,000 molecular weight such as is obtainable from the Enjay Company, Inc., 15 West Fifty-First Street, New York City, New York, under the name of Vistanex LM-MH, is dissolved in approximately 4 volumes of a chlorinated hydrocarbon solvent, as for example carbon tetrachloride, and gaseous oxygen is bubbled through the solution at ordinary temperatures. Approximately 0.16 part by weight of  $\text{PCl}_3$  per part of polymer is added dropwise to the reaction mixture over a period of about 3.5 hours. At this rate of addition the temperature of the reaction mixture increases from about 22° C. to about 28° C. Blowing with oxygen is continued for an additional 1.5 hours. The resulting yellowish oil is poured into approximately 2 volumes of water with rapid stirring to effect hydrolysis. The water layer is then decanted and the solvent layer washed twice with water to remove unreacted  $\text{PCl}_3$  and hydrolysis products. To the product is then added sufficient concentrated NaOH solution to neutralize the reaction mixture and approximately 2 parts by weight of a paraffinic mineral lubricating oil having a V.I. of 85, and a viscosity of 91.25 S.U.S. at 100° F. and 38.38 seconds at 210° F. and 4 parts by weight of a hydrocarbon solvent boiling in the range of 50 to 125° C. is also added. The resulting emulsion is stirred and heated on a hot plate for approximately 12 hours to a maximum temperature of 90° C. At this time water and carbon tetrachloride are substantially completely vaporized. The temperature is then raised to 150° C. over a period of approximately 1 hour with fuel gas being blown over the surface of the

reaction mixture to effect removal of the hydrocarbon solvent. An additional 2 parts by weight of the above lubricating oil are added, the product cooled and filtered through a filter aid and there is obtained a clear yellow viscous oil consisting of a solution of about 35% by weight of the sodium salt of the acid reaction product in mineral lubricating oil. This product has a sulfate ash of 0.38%.

The effectiveness of this product in improving the V.I. and the viscosity of an oil is indicated by the fact that when sufficient of the above additive is added to the same oil used in preparing the additive to impart a metal salt content of 8% the V.I. is increased from 85 to 138. The S.U. viscosity at 100° F. of the base oil is increased from 91.25 to 241.1 seconds and the viscosity at 210° F. is increased from 38.38 to 54.96 seconds.

In preparing the oil-soluble metal salts of reaction products using other olefin polymers, as for example propylene polymers, or copolymers of mono- and diolefins as for example propylene-butadiene copolymers, butylene-isoprene copolymers and the like, the procedure outlined hereabove is used with equal success.

To produce the compositions suitable for addition to mineral lubricating oils in which the initial reaction product with phosphorus chloride and oxygen is further reacted with a phosphorus sulfide, the above-described procedure is modified in that prior to hydrolysis and neutralization approximately 2 parts of relatively low viscosity paraffinic lubricating oil per part of initial polymer is added and the initial solvent as for example carbon tetrachloride is vaporized. The resulting product is heated for about 5 hours to a temperature between about 150° C. and about 200° C. with between about 2% and about 10% by weight, based on the polymer of a phosphorus sulfide such as phosphorus pentasulfide. At the end of this treatment the product is filtered and neutralized, as for example with sodium hydroxide by heating it for a period of 8-10 hours to a maximum temperature of 160° C. while adding strong aqueous sodium hydroxide solution portionwise. Additional quantities of mineral oil may be added so that the resulting product will contain between about 20% and about 50% by weight of oil-soluble metal salt and the product is filtered.

In the event it is desired to impart alkaline reserve to the above-described additive materials, additional quantities of base are added as for example between about 0.2 and about 3 equivalents of base per equivalent of metal salt, and the product is heated and dehydrated. Generally greater quantities of the excess base are solubilized by the metal salt if a catalyst or activator is present, such as a phenolic compound. In order to obtain the products of high metal content or as referred to herein having alkaline reserve, the methods described in U.S. Patents No. 2,616,904-5-6, 2,616,924-5, and 2,617,049 may be employed with success.

Solvents to be used in the preparation of the initial phosphorus trichloride reaction products include the various low boiling chlorinated hydrocarbon solvents such as carbon tetrachloride, chloroform, perchlorethylene and the like. Hydrocarbon solvents particularly the paraffinic hydrocarbon solvents are to be avoided because they are reactive under the conditions employed.

Mineral lubricating oils to be used in preparing the additives and in preparing the finished lubricants of this invention are paraffinic mineral lubricating oils having viscosity indices about 75 and preferably above 80. Usually solvent treated paraffinic oils will be used. The term "solvent treated" as used herein means that the oil has been extracted with a solvent that selectively removes the more naphthenic or aromatic portions of the lubricating oil stocks being treated leaving the more paraffinic portions as raffinates. Solvents such as SO<sub>2</sub>-benzene, phenol, cresols, furfural, etc. are used in such treatments. "Neutral oil," as the term is used herein, refers to a solvent treated, dewaxed western paraffinic distillate mineral

oil. Where this term is used in connection with a number, such as "90 neutral oil," the number is the nominal viscosity in Saybolt Universal seconds at 100° F.

Polymeric materials to be employed include polypropylene, polybutylene, and copolymers of propylene-butadiene, propylene-isoprene, butylene-butadiene, butylene-isoprene and similar products. Methods of preparation of such polymers and copolymers are well known in the art and need not be described. It is to be pointed out that in the case of the copolymers the ratio of olefin to diolefin is preferably above 2 to 1 and molecular weights of the polymers and copolymers as indicated hereabove will be between about 5,000 and about 200,000. Preferably they will have molecular weights between about 15,000 and about 50,000.

Phosphorus sulfides which may be used include, in addition to P<sub>2</sub>S<sub>5</sub>, which is distinctly preferred, P<sub>2</sub>S<sub>3</sub> and P<sub>4</sub>S<sub>7</sub>.

Metals which are useful in forming the oil-soluble metal salts of this invention include the alkali metals sodium, lithium and potassium, the alkaline earth metals calcium, strontium, barium and magnesium and some of the heavy metals such as zinc, copper, nickel. Of these the alkali and alkaline earth metals are preferred and the alkaline earth metals such as barium and calcium are particularly preferred. The metal salts may be made by direct neutralization of the acidic reaction products with a basic compound of the desired metal such as the oxide, hydroxide or carbonate of the metal. In some cases it may be advantageous to first form the sodium salt and then by metathesis convert the sodium salt to the desired metal salt. Such procedures are well known and need not be further described.

In preparing the finished lubricants of this invention the amount of oil-soluble metal salt or oil concentrate of metal salt to be employed will be that amount which is sufficient to impart the desired improvement in viscosity, V.I. and detergency characteristics. Generally between about 2% and about 15% of the oil-soluble metal salt will be used. The preferred range is possibly somewhat narrower as for example between about 4% and about 12%. The metal salts described are miscible in all proportions with the paraffinic lubricating oils and it is merely necessary to stir or agitate a mixture of the lubricating oil with the metal salts or oil concentrates of the metal salts to obtain a homogeneous product.

Amounts of PCl<sub>3</sub> to be used in forming the initial acidic reaction products will be between about 10% and about 30% by weight, and preferably between 15% and 20% by weight, based on the polymer or copolymer.

In the following examples which are to be considered as illustrative of the invention the engine tests used to determine detergency of the lubricating oils are the so-called Chevrolet Ex-1 test and the low temperature Lauson test. These tests are carried out as described below. Moreover the terminology with respect to SAE grades is that commonly used by the industry. Thus an oil referred to as SAE 10W-30 is one meeting the viscosity requirements for SAE 10W oils as well as SAE 30 oils.

The Chevrolet Ex-1 test is made in a standard Chevrolet, 6 cylinder overhead-valve engine, modified in that the top compression rings have four equally spaced vertical notches 0.125 inch wide and 0.009 inch deep, across the face of the rings. Special narrow slot oil rings are used on pistons 1, 3 and 5. The slot in these rings is 1/32 inch wide. The test is run for a total of 36 hours using the following test cycle which is repeated six times.

Cycle Portion	Time, hr.	Speed, r.p.m.	Load, b.h.p.	Temperatures, °F., Coolant Out	Oil
Part I.....	2	600	No load	125	120
Part II.....	2	2,500	45	95	185
Part III.....	2	2,500	45	200	245

Part I of the test cycle is run with a rich air-fuel ratio while Parts II and III are run with a normal air-fuel ratio.

Following completion of the 36-hour test run the engine is disassembled and the pistons, piston rings and other internal engine surfaces observed. Also the condition of the oil is noted. A rating of the detergency of the oil is made on the scale of 1 to 10 where 10 represents a substantially clean engine, free from sludge and deposits.

The low temperature Lauson engine test, which will be referred to herein as the Lauson test, is made in a single cylinder Lauson test engine using Babbitt bearings. The engine is operated for a total of 72 hours under a load of about 2.4 horsepower with a coolant temperature of 160° F. and an oil temperature of 150° F. At the end of the test, the cleanliness of the engine is observed and given a numerical detergency rating between 0 and 100%, where 100% indicates a perfectly clean engine. Thus, a detergency rating of 100 would indicate that there were substantially no lacquer or varnish-like deposits in the engine.

Example I

A solution of 333 grams of a polybutene of 30,000 molecular weight is dissolved in 2 liters of carbon tetrachloride and while stirring and bubbling oxygen through the solution 45 ml. of  $PCl_3$  is added dropwise over a period of 2.5 hours at a temperature range from 20° C. to 31° C. Some external cooling is employed in order to maintain the reaction mixture at these temperatures. Blowing with oxygen is continued for an hour following the addition of  $PCl_3$ . The resulting reaction product is poured into 3 liters of water with rapid stirring. The product is permitted to stratify, the water layer is discarded, and the solvent layer is washed twice with equal volumes of water. The water-washed product is added to 1332 grams of 90 neutral oil and 154 grams of 50% NaOH and the mixture heated and stirred for 12 hours at a temperature reaching 120° C., the temperature gradually being increased as the water and solvent vaporizes. Removal of solvent is completed by increasing the temperature to approximately 165° C. while blowing a stream of fuel gas onto the surface of the liquid. After filtering through a filter aid the product is a clear tan oil. This product has the following analysis.

	Percent by weight
Sulfated ash	1.11
P	.062
Cl	0.35
Polymer salt	20

A lubricating oil is prepared by dissolving 48% by weight of the above product in 90 neutral oil to give an oil containing 9.6% by weight of polymer. This lubricating oil has the following characteristics.

Sulfated ash, percent	0.36
S.U.S:	
100° F	309.1
210° F	60.92
0° F <sup>1</sup>	11,000
V.I	135
S.A.E. grade	10W-30

<sup>1</sup> Extrapolated.

In a Lauson engine test this oil shows a detergency of 93. In the same test the base oil alone, i.e. 90 neutral oil has a detergency of 60.

Example II

Example I is repeated with the modification that barium hydrate is used in place of sodium hydroxide to neutralize the acidic reaction product.

A lubricating oil made up by the dissolving 50% by weight of the oil concentrate of the barium polymer salt

in 90 neutral oil has substantially the same viscosity and V.I. as the product prepared from the sodium salt.

In the Lauson engine test this lubricating oil has detergency of 95.

Example III

To a solution of 2608 grams of a polybutene having a molecular weight of 30,000 in 2 gallons of carbon tetrachloride which is being blown with oxygen in an open stainless steel container is added 350 ml. of  $PCl_3$  over a period of 6.5 hours during which time the temperature of the reaction mixture is maintained between 19° C. and 31° C. Blowing with oxygen is continued for 1.5 hours, at which time the product is drenched with water and washed with additional portions of water in a glass agitator. To the washed carbon tetrachloride solution is added 200 ml. of water and a sufficient quantity of NaOH in the form of a 50% aqueous solution to maintain the pH above 8. The mixture is stirred and heated with air blowing at a temperature between 60° and 108° C. for 30 hours. During this treatment the temperature is maintained below the boiling point of the product. During this heating portions of 90 neutral oil are added at intervals to replace the solvent as it is evaporating in order to maintain an approximately constant volume. The preparation is finished in an additional 7 hours by heating to a maximum temperature of 150° C. with fuel gas blowing. A total of 627 grams of 50% NaOH and 7498 grams of 90 neutral oil is used. The resulting cloudy oil, referred to below as additive concentrate, is used in compounding two lubricating oils, both of which are filtered through a filter aid before testing. Both of these oils are tested in the Lauson engine and in the Chevrolet Ex-1 test.

Composition and test data on the two lubricating oils are summarized as follows.

	Oil No. M-4130	Oil No. M-4131
Composition:		
Polymer salt, percent	8.5	8.5
90 Neutral Oil, percent <sup>a</sup>	73.2	72.4
300 Neutral Oil, percent	18.3	18.1
Lubrizol 1060, percent <sup>b</sup>		1.0
Analysis:		
Sulfated Ash, percent	0.43	1.08
Phosphorus, percent	0.071	.207
Viscosity Data:		
SUS at 100° F	382.5	361.6
SUS at 210° F	65.74	64.0
SUS at 0° F <sup>c</sup>	18,000	16,000
V.I.	130	131
SAE Grade	20W-30	20W-30

<sup>a</sup> This value includes oil in the additive concentrate.

<sup>b</sup> An oil concentrate containing approximately 80% by weight of zinc dialkyl dithiophosphates obtainable from The Lubrizol Corporation of Cleveland.

<sup>c</sup> Extrapolated.

In the Lauson engine test oil number M-4130 has a detergency rating of 88.0 and in the Chevrolet Ex-1 test the detergency rating was 8.7. Oil number M-4131 had a detergency rating in the Lauson engine test of 98.7 and in the Chevrolet Ex-1 test of 8.2. For purposes of comparison a high quality 10W-30 heavy duty commercial lubricating oil had a detergency rating of 90 in the Lauson test and 7 in the Chevrolet Ex-1 test.

The used oils removed from the Chevrolet engine following the Ex-1 test show no appreciable changes in viscosity. The following viscosity data illustrate this.

	Oil No. M-4130		Oil No. M-4131	
	Unused	Used	Unused	Used
Viscosity Data:				
SUS at 100° F	382.5	383.1	361.6	333.7
SUS at 210° F	65.74	67.55	64.0	68.75
SUS at 0° F	18,000	16,000	16,000	16,000
V.I.	130	134	131	136
SAE Grade	20W-30	20W-30	20W-30	20W-30

## Example IV

The addition of a metal dithiophosphate, Lubrizol 1060 for example, to a lubricating oil containing the V.I. improving, detergent additive, such as was described in Example III, is done to improve the wear characteristics of the oil. This anti-wear effect is obtained in a more efficient manner by further reacting the polymer- $\text{PCl}_3\text{-O}_2$  reaction product of this invention with a phosphorus sulfide and converting that reaction product to its metal salt. In this way a single additive material is obtained which has the combined characteristics of imparting anti-wear, detergency and V.I. improvement to lubricating oils. The preparation of such an additive material is described below.

Example I is repeated to the stage where the reaction mixture is water washed. The water-washed carbon tetrachloride solution is added to 1332 grams of 90 neutral oil and the mixture is heated and stirred to  $120^\circ\text{C}$ . At this point, 75 grams of phosphorus pentasulfide is added and the mixture is heated and stirred at  $175^\circ\text{C}$ . for 3 hours under an atmosphere of dry nitrogen. Hydrogen sulfide is evolved during the early stages of the reaction. When the solution of  $\text{P}_2\text{S}_5$  is complete and evolution of  $\text{H}_2\text{S}$  has ceased, the mixture is cooled to  $120^\circ\text{C}$ . While stirring, a saturated aqueous solution containing 70 grams of barium hydroxide is added dropwise at a slow rate to minimize foaming. When this addition is completed the temperature of the mixture is again raised to  $175^\circ\text{C}$ . under an atmosphere of dry nitrogen to insure completion of the reaction. The oil solution of polymer salt is filtered hot to yield a concentrate of the following analysis:

	Percent by weight
Sulfated ash -----	3.0
P -----	0.4
Cl -----	0.3
S -----	0.6
Polymer salt -----	20

A lubricating oil prepared by dissolving 50% of the above concentrate in 90 neutral oil has the following characteristics:

Sulfated ash, percent -----	1.5
S.U.S., $100^\circ\text{F}$ . -----	314.2
S.U.S., $210^\circ\text{F}$ . -----	6230
S.U.S., $0^\circ\text{F}$ . (extrapolated) -----	11,500
V.I. -----	134
S.A.E. grade -----	10W-30
Lauson detergencies -----	92

## Example V

Example I is repeated using a polybutene of about 15,000 molecular weight. The resulting product is very similar to the products of Example I and III except for its poorer V.I. improving efficiency.

Approximately 15% of the polymer salt in 90 neutral oil is required to make a 10W-30 oil.

## Example VI

Example I is repeated with a polybutene of about 100,000 molecular weight. The resulting product is similar to that of Examples I and III except for its better V.I.-improving efficiency and poorer shear stability. Approximately 4% of the polymer salt is required to make a 10W-30 oil. For operations where shear stability is not important, this is an advantage of the higher molecular weight polymer. However, in operations such as those represented by the Ex-1 tests of Example III, the used oil viscosity at  $210^\circ\text{F}$ . drops as much as 10% from the original unused oil viscosity.

A lubricating oil prepared by dissolving sufficient of the above concentrate in 90 neutral oil to produce an oil containing 4% by weight of the polymer salt has a Lauson detergency of 93 and a V.I. of 135.

## Example VII

In the preparation of low pressure polypropylene, as by the use of Ziegler type catalysts, a mixture of intermediate and high molecular weight material is obtained. The intermediate molecular weight portion is soluble in the lower alkyl ethers, such as diethyl-, di-iso-propyl, or di-n-propyl ether. A polypropylene of this type is recovered from the processing of the mixture in the form of a clear, colorless, sticky resin. Its molecular weight is estimated as about 35,000 and its V.I.-improving efficiency is about the same as that of commercial polybutenes of equivalent molecular weight. This resin is reacted with  $\text{PCl}_3$  and oxygen by the method of Example I to recover a sodium polymer salt. The properties of this polymer salt are equivalent to those of the product of Example I.

## Example VIII

A copolymer is made by a process similar to that described in Example VII. It contains 98% propylene and 2% butadiene. This clear, colorless, sticky resin is reacted with  $\text{PCl}_3$  by the method of Example I and converted to the sodium polymer salt. The properties of the polymer salt are equivalent to those of Example I.

## Example IX

A copolymer of 95% isobutene and 5% isoprene is made in straight-run gasoline solution in a continuous unit at  $-78^\circ\text{C}$ ., using a trace of  $\text{BF}_3$  as a catalyst. The resulting gasoline solution is poured into two volumes of isopropyl alcohol to precipitate the polymer. The crude polymer is settled out and re-dissolved in one volume of carbon tetrachloride. This solution is poured into two volumes of isopropyl alcohol, and the polymer again separated by settling. The polymer, which has a molecular weight of about 25,000 is re-dissolved in carbon tetrachloride, water washed, and the solution dried by azeotropic distillation. The resulting polymer solution is reacted with  $\text{PCl}_3$  and worked up by the method of Example I to yield a polymer salt having properties similar to those of the product of that example.

## Example X

Example I is repeated except that a slurry of calcium hydroxide, freshly prepared by hydrating calcium oxide, is used instead of sodium hydroxide to produce a calcium salt of the acidic reaction products.

Oils prepared and test as described in Example I have substantially the same properties and characteristics as those set forth in that example.

The foregoing description and examples of this invention are to be considered as illustrative of the invention and are not to be taken as limiting the invention to the particular additive materials specifically shown, since other materials may be employed to produce lubricating oils having the characteristics described as would be apparent to one skilled in the art.

I claim:

1. A composition of matter adapted for addition to mineral lubricating oil to impart improved V.I. and detergent characteristics to said oil composition comprising a mineral oil solution of an oil-soluble metal salt of the acidic reaction product obtained by reacting an aliphatic hydrocarbon polymeric material having a molecular weight between 5000 and 200,000 and selected from the class consisting of the olefin polymers, polypropylene and polybutylene, and the copolymers of propylene-butadiene, propylene-isoprene, butylene-butadiene and butylene-isoprene with between about 10% and about 30% by weight of phosphorus trichloride in the presence of gaseous oxygen at a temperature between about  $10^\circ\text{C}$ . and about  $100^\circ\text{C}$ . and hydrolyzing the resulting product, said composition containing greater than about 15% by weight of said oil-soluble metal salt.

2. A composition according to claim 1 in which the metal of the metal salt is an alkaline earth metal.

3. A composition according to claim 1 in which the metal of the metal salt is barium.

4. A composition according to claim 1 in which the metal of the metal salt is an alkali metal and said composition contains about 35% by weight of said metal salt.

5. A composition according to claim 1 having alkaline reserve in which said oil-soluble metal salt is further reacted with 0.2 to 3 equivalents of base per equivalent of metal salt in the presence of a phenolic activator.

6. A method of preparing a composition of matter adapted for addition to mineral lubricating oil which comprises reacting a hydrocarbon polymeric material having a molecular weight between 5000 and 200,000 and selected from the class consisting of the olefin polymers, polypropylene and polybutylene, and the copolymers of propylene-butadiene, propylene-isoprene, butylene-butadiene and butylene-isoprene dissolved in an inert solvent with between about 10% and about 30% by weight of phosphorus trichloride at a temperature between about 10° C. and about 100° C. while bubbling gaseous oxygen through the reaction mixture, hydrolyzing the resulting product, replacing said solvent with mineral lubricating oil and neutralizing the reaction mixture with a metal base.

7. A method according to claim 6 wherein prior to the hydrolyzing step said solvent is replaced with mineral lubricating oil and the oil solution of reaction product is further treated with between about 2% and about 10% by weight, based on the original polymeric material, of a phosphorus sulfide at a temperature between about 150° C. and about 200° C.

8. A composition of matter adapted for addition to mineral lubricating oil to impart improved V.I. and detergent characteristics to said oil composition comprising a mineral oil solution of an oil-soluble metal salt of the acidic reaction product obtained by reacting an aliphatic hydrocarbon polymeric material having a molecular weight between 5000 and 200,000 and selected from the class consisting of the olefin polymers, polypropylene and polybutylene, and the copolymers of propylene-butadiene, propylene-isoprene, butylene-butadiene and butylene-isoprene with between about 10% and about 30% by weight of phosphorus trichloride in the presence of gaseous oxygen as a temperature between about 10° C. and about 100° C., and further reacting said product with between 2% and about 10% by weight of a phosphorus sulfide at a temperature between 150° C. and 200° C. and hydrolyzing the resulting product, said composition containing between about 20% and about 50% by weight of said oil-soluble metal salt.

9. A high V.I. detergent lubricating oil composition containing a major proportion of mineral lubricating oil and a small amount sufficient to impart detergency and

high V.I. characteristics to said oil of an oil-soluble metal salt of the acidic reaction product obtained by reacting an aliphatic hydrocarbon polymeric material having a molecular weight between 5000 and 200,000 and selected from the class consisting of the olefin polymers, polypropylene and polybutylene, and the copolymers of propylene-butadiene, propylene-isoprene, butylene-butadiene and butylene-isoprene, with between about 10% and about 30% by weight of phosphorus trichloride in the presence of gaseous oxygen at a temperature between about 10° C. and about 100° C. and hydrolyzing the resulting product.

10. A lubricating oil according to claim 9 in which the metal of the metal salt is an alkaline earth metal.

11. A lubricating oil according to claim 9 in which the metal of the metal salt is barium.

12. A lubricating oil according to claim 9 in which the metal of the metal salt is an alkali metal.

13. A lubricating oil according to claim 9 in which the amount of oil-soluble metal salt is between about 2% and about 15% by weight based on the mineral lubricating oil.

14. A high V.I., detergent, lubricating oil composition containing a major proportion of mineral lubricating oil and a small amount sufficient to impart detergency and high V.I. characteristics to said oil of an oil-soluble metal salt of the acidic reaction product obtained by reacting an aliphatic hydrocarbon polymeric material having a molecular weight between 5000 and 200,000 and selected from the class consisting of the olefin polymers, polypropylene and polybutylene, and the copolymers of propylene-butadiene, propylene-isoprene, butylene-butadiene and butylene-isoprene, with between about 10% and about 30% by weight of phosphorus trichloride in the presence of gaseous oxygen at a temperature between about 10° C. and about 100° C., further reacting said product with between about 2% and about 10% by weight of phosphorus pentasulfide at a temperature between about 150° C. and about 200° C. and hydrolyzing the resulting product.

15. A lubricating oil according to claim 14 in which said oil-soluble metal salt is further reacted with between 0.2 and 3 equivalents of metal base per equivalent of metal salt in the presence of a phenolic activator to impart alkaline reserve to said lubricating oil.

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