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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 phosphorus-containing reaction products obtained by reacting high molecular weight olefin-diolefin copolymers with a dialkyl hydrogen phosphite 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 engines, 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

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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 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 a dialkyl hydrogen phosphite with 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. The polymeric material to be used is a copolymer of an olefin with a diolefin. The reaction is effected at a temperature generally between about 75° C. and about 225° C. in the presence of a peroxide type catalyst. 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 further in oil-soluble metal salts of the type 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 aliphatic copolymers, as for example a polymerized mixture of isobutene and isoprene having a molecular weight of approximately 25,000 is dissolved in an equal volume of a light straight-run gasoline. To this mixture is added approximately 1 volume per volume of polymer of 90 neutral oil. To this mixture is added approximately 0.16 part by weight of diethyl hydrogen phosphite per part of copolymer together with a small amount, as for example 0.015 part of catalytic material such as di-tertiarybutyl peroxide. The mixture is then heated under reflux for approximately two hours and subsequently vacuum distilled to a bottoms temperature of 165° C. at 1.2 mm. Hg pressure to remove solvent and unreacted diethyl hydrogen phosphite. The resulting product may be hydrolyzed and converted into a metal salt by reaction with a metal base, as for example barium hydrate, in the presence of water. This hydrolysis and conversion to the metal salt is preferably effected at refluxing temperatures, water being removed by means of a water trap in the reflux line. Following dehydration the product may be filtered to remove solid materials, additional lubricating oil added and any remaining solvent then removed by evaporation or vacuum distillation.

Hydrolysis of the initial reaction product and conversion of the hydrolyzed product to its metal salt may also be carried out using acid hydrolysis. Thus the initial product of reaction of the polymer with the phosphite

ester can be hydrolyzed by treatment with concentrated HCl. The mixture is stirred and heated on a steam bath in an open container. Following this treatment the aqueous phase is permitted to separate and is discarded. The solvent phase containing the acidic polymer material is then reacted with a metal base as for example barium hydroxide and the salt recovered as an oil concentrate as described above. Following this method of hydrolysis generally higher proportions of metal in the form of metal salt are obtained in the product.

Each of the above copolymer salt concentrates when added to additional mineral lubricating oil (90 neutral oil) to produce lubricating oils containing approximately 8% by weight of the copolymer salt produce lubricating oils of high detergency and high V. I. The V. I. of the base oil was 85 and after adding the copolymer salt it increased to approximately 138 in each instance.

The proportion of metal salt in the oil concentrate, i. e. the additive of this invention, may vary between about 15% and 50% by weight depending upon the amount of lubricating oil employed in its preparation.

The term "neutral oil" as used herein refers to a solvent-treated, dewaxed, Western paraffinic distillate mineral oil. When 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.

The reaction mechanism involved and the reaction products obtained by reacting olefin-diolefin copolymers with dialkyl hydrogen phosphites are not fully understood. It is believed that reaction occurs at the residual double bonds present in the copolymers but reaction may occur at other points in the copolymer molecules. Moreover it is believed that the dialkyl phosphites react to first give phosphorus ester derivatives although the structure of such derivatives has not been definitely established. It is known that following the initial reaction between copolymer and dialkyl phosphite the product is capable of being converted to a metal salt if the product is first hydrolyzed or if the salt is formed under conditions which would normally effect hydrolysis of esters or ester like compounds. As shown by the preceding description the hydrolysis may be effected under alkaline or acid conditions. It is not essential that the various reaction products described herein be capable of identification by structure or formula since they can be produced following the procedures fully described herein.

In preparing the oil-soluble metal salts of reaction products using other copolymers of mono- and diolefins as for example propylene-butadiene and propylene-isoprene copolymers, butylene-butadiene copolymers and the like, the procedure outlined hereinabove is used with equal success. It is to be pointed out that the ratio of olefin to diolefin is preferably above 2 to 1 and may be as high as 99 to 1. Generally the ratio will be between about 5 and about 98 to 1. Molecular weights of the copolymers as indicated hereinabove will be between about 5,000 and about 200,000. Preferably they will have molecular weights between about 10,000 and about 50,000.

The dialkyl hydrogen phosphites to be used to react with the copolymers according to this invention include, in addition to diethyl hydrogen phosphite which is preferred, those compounds in which the alkyl groups each contain 1 to 4 carbon atoms. Thus the alkyl groups may be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tert-butyl radicals. Moreover, the alkyl groups present in the phosphite molecule may be the same or different. The amount of dialkyl hydrogen phosphite to be used will be between 0.05 part and 0.5 part per part of copolymer.

Catalysts to be used in effecting the reaction between the copolymer and the phosphite include the various organic peroxides and hydroperoxides such as benzoyl peroxide, methyl ethyl ketone peroxide, peracetic acid, di-tertiary butyl peroxide, tertiary butyl hydroperoxide, cumene hydroperoxide, p-methane hydroperoxide, perox-

idized gasoline, methyl cyclohexyl hydroperoxide and the like. While the amount of catalyst to be used is not critical it is found that amounts of organic peroxide between 0.005 part and 0.1 part per part of copolymer give satisfactory results.

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 and tin. 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 obtained by hydrolyzing the initial reaction products or as otherwise described hereinabove using 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 the event it is desired to impart alkaline reserve to the above-described additive materials, additional quantities of metal base are added to the oil concentrates of metal salt 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. The metal of the metal base used to impart alkaline reserve will be one of the alkali or alkaline earth metals described above. Generally greater quantities of excess metal 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 as having alkaline reserve, the methods described in U. S. Patents Nos. 2,616,904-5-6, 2,616,924-5, and 2,617,049 may be employed with success. For example to 1 part of the metal salt-oil concentrate is added about 0.02 to 0.1 part of an alkyl-substituted phenol, e. g., p-tert-butyl phenol and the mixture heated to 95° C. with stirring. The desired amount of metal base, e. g., barium hydrate as a slurry in water is added and the mixture heated to about 150° C. over a period of about 2 hours to vaporize the water. The resulting product is filtered. This procedure is effective with alkali metals as well as with the divalent metals such as alkaline earth metals illustrated.

Mineral lubricating oils to be used in preparing the additives, i. e. the metal salt-oil concentrates, and in preparing the finished lubricants of this invention are paraffinic mineral lubricating oils having viscosity indices above 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 SO₂-benzene, phenol, cresols, furfural, etc. or mixtures of such solvents are used in such treatments.

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.

Olefin-diolefin copolymers are well known and methods of preparing them are also known in the art. Some of the copolymers used in preparing the additives of this in-

vention have been prepared in a continuous reactor consisting of a coil made of approximately 18 feet of 0.25 inch copper tubing. This coil is placed in a bath and cooled with Dry Ice and acetone or by other refrigerant means. In a typical preparation 1 part of a solvent such as a light gasoline stock boiling in the range of approximately 125° F.-260° F. containing the desired proportion of diolefin such as isoprene is pumped into the coil reactor in a bath maintained at about -75° C. At the same time approximately 0.2 part of an olefin, e. g., isobutylene is pumped through a secondary inlet into the coil and mixed with the isoprene and gasoline. By the time this mixture is cooled to approximately bath temperature a catalyst mixture consisting of 10% of BF₃ in ethane is injected into the coil and the product leaving the coil, after a residence time of approximately 30 seconds following the injection of the catalyst mixture consists of a gasoline solution of copolymer. The solvent, reactants and catalyst are pumped continuously into the coil using about the proportion of solvent indicated. The proportion of catalyst is varied depending upon the molecular weight of the copolymer desired. It is found that by operating the reactor so that the temperature of the reaction mixture following addition of catalyst is -68° F. and feeding 2050 ml. of gasoline solvent containing 6 grams of isoprene, 400 ml. of isobutylene, and 10 g. BF₃ in 90 ml. of ethane per hour the product copolymer has a molecular weight of about 25,000. If a higher molecular weight copolymer is desired, such as one having a molecular weight in the range of 60,000 to 70,000, this can be obtained using the same proportions of ingredients by maintaining a reaction temperature of about -100° C. On the other hand if a lower molecular weight polymer such as one having a molecular weight of 10,000 to 12,000 is desired, a reaction temperature of -42 to -44° C. will be employed. Other factors also affect molecular weights of the copolymers. Thus the ratio of diolefin to olefin, the amount of catalyst and the kind of olefin and/or diolefin employed all influence the molecular size of the copolymer.

Olefins described herein as being useful in preparing the copolymers include propylene, butylene and isobutene. These are C₃ and C₄ olefins. Diolefins described herein as being useful in preparing the copolymers include butadiene and isoprene. These are C₄ and C₅ diolefins, respectively. It is thus the copolymers of a C₃ or C₄ olefin with a C₄ or C₅ diolefin which are shown to be reacted with dialkyl hydrogen phosphites in preparing the additives of this invention.

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 54 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

To 1000 g. of a gasoline solution containing approximately 34% of an isobutene-isoprene copolymer having a molecular weight of approximately 26,000 and prepared in the coil reactor described hereinabove at a temperature of -68° C. using a reacting ratio of isobutene to isoprene of approximately 98.5 to 1.5 is added 340 g. of 90 neutral oil and the mixture is distilled to a bottoms temperature of 140° C. to remove a portion of the gasoline. The bottoms fraction is cooled and to it is added 55 grams of diethyl hydrogen phosphite and 5 ml. of di-tertiary-butyl peroxide. The mixture is heated under reflux for 2 hours and then vacuum distilled to a bottoms temperature of 165° C. at 1.2 mm. Hg pressure to remove solvent and unreacted phosphite. The resulting product is a light brown oily concentrate of the copolymer phosphite reaction product in oil. Approximately 679 grams of this material is recovered. This product will be referred to as product A.

Product A is separated into 2 equal portions and one-half of it is dissolved in 100 ml. of a paraffinic solvent having a boiling range of 90 to 140° F. and to it is added 105 grams Ba(OH)₂·5H₂O and 200 ml. of water and this mixture is refluxed for 1.5 hours after which a water trap is inserted in the reflux line and distillation continued for an additional 8 hours to remove the water. During the water removal step an additional 300 ml. of solvent is added to maintain volume. The resulting product is filtered through a diatomaceous earth filter aid, an additional 170 grams of 90 neutral oil is added to the filtrate and the solvent then removed by vacuum distillation. The product amounts to 531 grams of a clear opalescent oily concentrate containing 33.3% polymer salt and having a sulfate ash content of 0.37%. This product will be referred to as product B.

The remaining portion of product A is dissolved in 100 ml. of paraffinic solvent described above and to it is added 50 ml. of 38% HCl and 100 ml. of water. This mixture was heated with stirring on a steam bath in an open beaker for 2 hours. The naphtha layer is separated and washed 3 times with water at 50-60° C. to remove excess HCl and then refluxed 2 hours with a solution of 105 grams of Ba(OH)₂·5H₂O in 200 ml. of water. The resulting product is dehydrated by reflux distillation using a water trap and filtered by suction using a diatomaceous earth filter aid. An additional 170 grams of 90 neutral oil is added to the filtrate and the solvent then removed by vacuum distillation. This product amounting to 528 grams will be referred to herein as product C. Analysis shows it to contain 33.3% polymer salt and to have a sulfate ash of 1.23%.

Lubricating oils were made from products B and C by dissolving in each instance about 26% of the products in

90 neutral oil. Data regarding these two lubricating oils are as follows:

	Lubricating Oil Prepared From	
	Product B	Product C
Polymer salt in oil, percent.....	8.8	8.2
Sulfate ash in oil, percent.....	0.04	0.18
Viscosity, SUS:		
100° F.....	264	254
210° F.....	56.5	55.1
V. I.	135	133
SAE Grade.....	10W-20	10W-20
Detergency rating *:		
Lauson test.....	81	80
Chevrolet Ex-1 test.....	S. 1	S. 0

* The base oil, 90 neutral oil, has a detergency rating of 30 in the Lauson test. In the Chevrolet Ex-1 test, a direct comparison could not be made with base oil alone. After 38 hours on the operating cycle, the pistons seized and the engine could not be re-started. The piston lacquer was sufficient to stop the engine.

The viscosities of the used oils from the Chevrolet Ex-1 test are substantially the same as those of the oil before test indicating good shear stability of the polymer salt.

Example II

A gasoline solution of an isobutene-isoprene copolymer having a molecular weight of 12,000 is prepared in a continuous manner in the coil reactor previously described by feeding to the reactor the following reactants in the amounts indicated:

	Quantity per hour
Solvent (gasoline).....	ml. 2050
Isoprene	g. 40
Isobutene	g. 400
BF ₃ (10% in ethane).....	g. 10

The reaction temperature is maintained at 65° C. with a bath temperature of -78° C.

To 1000 grams of this product is added 340 grams of 90 neutral oil and the mixture distilled to a bottoms temperature of 140° C. to remove part of the solvent. To the cooled bottoms fraction is added 55 grams of diethyl hydrogen phosphite and 5 ml. of ditertiary butyl peroxide. The mixture is heated under reflux for 2 hours and then vacuum distilled to a bottoms temperature of 165° C. at 1.2 mm. Hg pressure. The resulting bottoms material is a light colored oily concentrate of the copolymer phosphite reaction product in oil.

The above product is converted to its sodium salt by the method used to prepare product B, Example I, except that an equivalent amount of NaOH was used in place of the barium hydrate.

The resulting oil concentrate of polymer salt is found to contain 32.5% polymer salt, it has a sulfate ash of 0.18% and contains 0.16% phosphorus. A lubricating oil prepared by dissolving 24.6% of this concentrate in a 3/1 blend of 90 neutral oil and 300 neutral oil has a V. I. of 140, a Lauson detergency of 88 and a Chevrolet Ex-1 detergency of 8.2. It meets the requirements of SAE grade 10W-20.

Example III

Example II is repeated using an isobutene-4% butadiene copolymer having a molecular weight of 10,000 in place of the isobutene-isoprene copolymer. A lubricating oil containing 14% by weight of the potassium copolymer salt in 90 neutral oil has a Lauson detergency of 84 and a V. I. of 132.

Example IV

A propylene-butadiene copolymer is made by pumping a mixture of 94% propylene and 6% butadiene into a rocking pressure vessel containing a suspension of a mixed aluminum alkyl-titanium tetrachloride Ziegler-type catalyst in toluene. Pumping is at such a rate that the pres-

sure rise is controlled at below 2 atmospheres. When approximately 1 kilogram of gaseous mixture has been added to 10 grams of catalyst in 1 liter of toluene, the reaction is stopped. The resulting polymer solution is removed from the reactor and washed with water and methanol. The toluene is evaporated and the copolymer fractionated by extraction with diisopropyl ether to separate the intermediate polymeric material of about 25,000 molecular weight. This propylene-butadiene copolymer is reacted by the method C of Example I, except that strontium hydroxide is used to neutralize the hydrolyzed product. A concentrate containing 33.3% polymer salt and a sulfate ash of 1.7% is recovered. A lubricating oil prepared by dissolving this concentrate in 90 neutral oil to give a finished oil containing 8.5% polymer salt has a V. I. of 142, and a Lauson detergency of 86. It meets the requirements of SAE grade 10W-30.

Example V

To 200 grams of the product C of Example I are added 8 grams of p-tertiary-butyl phenol. The mixture is heated and stirred at 95° C. while a slurry of 7 grams of barium hydroxide pentahydrate crystals in a minimum amount of water is slowly added. The mixture is then heated with continuous stirring to 150° C. to remove the water. The resulting product is filtered hot by suction, using a diatomaceous earth filter aid. Analysis of the resulting alkaline reserve product shows it to contain 32.0% polymer salt and to have a sulfate ash of 3.6%. It has a base number of 48. A lubricating oil prepared from it containing 8.5% polymer salt has a V. I. of 134 and a Lauson detergency of 90.

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 consisting essentially of mineral lubricating oil containing 15% to 50% of an oil-soluble metal salt of the product obtained by reacting an olefin-diolefin copolymer having a molecular weight between 5,000 and 200,000 with a dialkyl hydrogen phosphite in which the alkyl groups each contain 1 to 4 carbon atoms at a temperature between 75° C. and 225° C. in the presence of an organic peroxide catalyst and hydrolyzing the reaction product said copolymer being a copolymer of a C₃ to C₄ olefin with a C₄ to C₅ diolefin.

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.

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 an alkyl-substituted phenol.

6. A method of preparing a composition of matter adapted for addition to mineral lubricating oil which comprises reacting an olefin-diolefin copolymer having a molecular weight between about 5,000 and about 200,000 dissolved in mineral lubricating oil and hydrocarbon solvent with between about 0.05 and 0.5 part per part of copolymer of a dialkyl hydrogen phosphite at a temperature between about 75° C. and about 225° C. in the presence of an organic peroxide, hydrolyzing the resulting product and converting the hydrolyzed product to its metal salt said copolymer being a copolymer of a C₃ to C₄ olefin with a C₄ to C₅ diolefin.

7. A high V. I. detergent lubricating oil composition comprising 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 product obtained by reacting an olefin-diolefin copolymer having a molecular weight between 5,000 and 200,000 with a dialkyl hydrogen phosphite in which the alkyl groups each contain 1 to 4 carbon atoms at a temperature between 75° C. and 225° C. in the presence of an organic peroxide catalyst and hydrolyzing the reaction product said copolymer being a copolymer of a C₃ to C₄ olefin with a C₄ to C₅ diolefin.

8. A lubricating oil according to claim 7 in which the metal of the metal salt is an alkaline earth metal.

9. A lubricating oil according to claim 7 in which the metal of the metal salt is barium.

10. A lubricating oil according to claim 7 in which the metal of the metal salt is an alkali metal.

11. A lubricating oil according to claim 7 in which the amount of oil-soluble metal salt is between about 2% and about 15% by weight based on the mineral lubricating oil.

12. A lubricating oil according to claim 7 in which said copolymer is an isobutylene-isoprene copolymer having a molecular weight between 10,000 and 50,000.

13. A lubricating oil according to claim 7 in which said oil-soluble metal salt is further reacted with 0.2 to 3 equivalents of metal base per equivalent of metal salt in the presence of an alkyl-substituted phenol.

14. A high V. I. detergent lubricating oil consisting es-

entially of mineral lubricating oil containing between about 2% and about 15% by weight of an oil-soluble metal salt of the product obtained by reacting an olefin-diolefin copolymer having a molecular weight of 10,000 to 50,000 in the presence of mineral lubricating oil with between about 0.05 and about 0.5 part per part of copolymer of a dialkyl hydrogen phosphite in which the alkyl groups each contain 1 to 4 carbon atoms at a temperature between 75° C. and 225° C. in the presence of an organic peroxide catalyst and hydrolyzing the reaction product said copolymer being a copolymer of a C₃ to C₄ olefin with a C₄ to C₅ diolefin.

15. A lubricating oil according to claim 14 in which said copolymer is prepared from a mixture of olefins and diolefins containing a ratio of between 2 and 99 parts of olefin per part of diolefin.

16. A lubricating oil according to claim 14 in which said copolymer is an isobutene-isoprene copolymer containing 98.5 parts of isobutene and 1.5 parts of isoprene.

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