United States Patent Office 3,003,959 Patented Oct. 10, 1961

3,003,959

LUBRICATING OIL ADDITIVES AND LUBRICATING OILS CONTAINING THE SAME

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No Drawing. Filed Dec. 21, 1959, Ser. No. 860,677
14 Claims. (Cl. 252—32.7)

This invention relates to lubricating oil additives and particularly concerns additives adapted for addition to mineral lubricating oils to produce lubricating oil compositions of a high viscosity index having excellent detergent, dispersant and anticorrosion characteristics. The invention further relates to lubricating oil compositions containing such additives.

Among the requisite characteristics of lubricating oil compositions suitable for use in modern gasoline engines, particularly of the spark ignition type, are high viscosity index, detergent, dispersant and anticorrosion properties. The viscosity index (V.I.) of an oil is a measure of the extent to which the viscosity of the oil changes with temperature, high V.I. oil being one whose viscosity changes only slightly with change in temperature. The property of detergency is one of preventing the formation of carbonaceous and/or varnish-like deposits from accumulating on the various internal parts of the engine, e.g., on pistons and cylinder walls, in piston ring grooves, etc. The property of dispersion is one of preventing deposition of sludge in the form of a pasty or semi-fluid mass on various surfaces within an engine. Such surfaces include rocker arm assemblies, rocker arm cover, push rod cover, oil screen, crankcase oil pan, push rod chamber and valve top deck. The property of anticorrosiveness is one of preventing the formation and/or accumulation in the oil of acidic bodies which attack the metal parts of the engine under conditions of use. Since no mineral lubricating oil itself possesses all of these properties to the extent required by modern high performance engines, they are attained by incorporating minor amounts of various agents, generally referred to as lubricating oil additives or additive concentrates, into a suitable base oil. Many attempts have been made to prepare a single additive which is capable of imparting all of the aforementioned characteristics to the base oil, but for the most part such so-called all-purpose additives have not proved entirely satisfactory. Moreover, even though several additives are employed with the object of making the lubricating oil suitable for use in spark ignition engines, particularly automotive engines used in stop-and-go driving, they generally leave something to be desired with respect to some of the characteristics, at least to the extent considered necessary by automobile manufacturers and the oil industry.

Among the many additives disclosed by the prior art are the metal salts and in some cases the superbased metal salts of acidic compounds prepared by reacting a phosphorus sulfide, e.g., phosphorus pentasulfide with a hydrocarbon oil or with a hydrocarbon polymer, e.g., polyisobutylene or a hydrocarbon copolymer, e.g., isobutylene-butadiene copolymer, or polymers produced by polymerizing cracked products obtained during oil refining. Certain of such products have proved reasonably satisfactory from a standpoint of imparting the requisite detergency characteristics and, where polymers are concerned, the required viscosity index. Moreover, some of such products have been found to impart satisfactory anticorrosion properties, and furthermore, in some instances sufficient dispersive properties to prevent objectionable deposits of sludge in the engine. However, of the above compounds the only ones which are capable of imparting to lubricating oil all of the characteristics described herein as being necessary and of imparting these characteristics to the desired degree are those obtained by treating certain hydrocarbon copolymers with a phosphorus sulfide and neutralizing and superbasing the resulting acidic products. Although the prior art has taught the preparation of some of such compounds and their use in lubricating oil has been taught in a general way, it is found that many of the compositions within such teaching cannot be made and if made are not soluble in mineral lubricating oils. Thus, oil solutions of many of the products obtained by reacting a hydrocarbon copolymer, e.g., a copolymer of a monoolefin and a diolefin, with a phosphorus sulfide and neutralizing the resulting acidic product cannot be superbased by treatment with excess base, e.g., an alkaline earth metal base, because the products gel and form a mass which is not filterable even at elevated temperatures and which is not soluble in further quantities of lubricating oil. It has been found that when an agent such as an alkyl-substituted phenol, as described in U.S. Patents 2,695,910, 2,767,164 and 2,767,209, is used as an aid to superbasing, the amount of gelling or the tendency to gel is reduced, but that this technique still does not permit the superbasing of many of the compositions which have been described in the art as being suitable for treatment in this manner in the production of lubricating oil additives.

It is accordingly an object of this invention to provide a single additive material capable of imparting to mineral lubricating oil an exceptional degree of detergency and dispersiveness together with anticorrosion and high viscosity index characteristics.

It is another object of this invention to prepare a lubricating oil additive having the above mentioned properties by reacting a phosphorus sulfide with a copolymer of a monoolefin and a diolefin.

It is still another object of this invention to provide a method of preparing a lubricating oil additive having all of the above characteristics.

It is a further object of this invention to provide an equation by means of which it is possible to predict whether a given lubricating oil additive composition can be prepared and thus an equation which defines compositions which are sufficiently oil-soluble to prevent gelation during neutralization and superbasing.

A further and more general object is to provide lubricating oil compositions having all of the above indicated characteristics.

Other and related objects will be apparent from the following detailed description of the invention and various advantages not specifically referred to herein will occur to those skilled in the art upon employment of the invention in practice.

We have now found that the above objects and attendant advantages may be realized by reacting a phosphorus sulfide, e.g., phosphorus pentasulfide with certain hydrocaron copolymers and then reacting the acidic products so obtained with an alkaline earth metal base in the presence of an alkylated phenol as a solubilizing agent permitting incorporation of amounts of alkaline earth metal base greater than those required to neutralize the acidic reaction products. The resulting product may or may not be blown with CO_2 to improve their compatibility in oil with certain other additive materials. Products obtained in this manner are capable of imparting to mineral lubricating oil the desired detergent, dispersant, anticorrosion and V.I. characteristics. The exact nature of the phosphorus- and sulfur-containing copolymer reaction products, the manner in which the excess alkaline earth metal base is combined therewith, and the function of the alkyl phenol in solubilizing the excess base are not known and accordingly the additives of the present

invention must be described and claimed by their manner of preparation rather than as definite chemical entities. The invention thus consists in lubricating oil additives prepared from certain hydrocarbon copolymers of olefins and diolefins, a phosphorus sulfide, an alkyl phenol and an alkaline earth metal base and in lubricating oil compositions comprising such additives.

In order to obtain lubricating oil additives and lubricating oils of this invention using the mentioned reactants and having all of the desired characteristics, it is essential that the copolymers be of a specific type and have a molecular weight within certain limits; the amount of phosphorus sulfide used to react with the copolymers must be controlled within certain limits; and the amount of alkyl phenol employed must also be controlled. The reactants and the proportions in which they are used are described more fully herebelow. In all of the description which follows and in the examples where the proportions of materials are expressed in parts, it is meant parts by weight.

HYDROCARBON COPOLYMERS

The hydrocarbon copolymers which are employed as starting materials are copolymers of isobutylene with isoprene. The isobutylene and isoprene may be employed in more or less pure form (in which case they are usually polymerized in the presence of an inert liquid polymerization medium) or they may be employed in admixture with inert components. For example, in preparing a typical copolymer for use in accordance with the invention, the isobutylene may be provided in relatively pure form or it may be employed in the form of a mixture of isobutylene and butane, such as is produced as a by-product from petroleum refining processes. Similarly, the isoprene may be employed in relatively pure form or it may contain inert ingredients.

The polymerization reaction is effected at low temperatures, e.g., at from about −30° C. to about −100° C., preferably from about −50° C. to about −80° C., under the influence of a Friedel-Craft type catalyst such as aluminum chloride, aluminum bromide, zinc chloride, boron trifluoride, titanium tetrachloride, etc., and preferably in the presence of an inert liquid hydrocarbon or halogenated hydrocarbon reaction medium. In general, conventional techniques, such as those described in U.S. Patent No. 2,356,128, are employed, and the various process variables are controlled in the known manner to produce a polymeric product whose molecular weight is between about 10,000 and about 150,000. Conveniently, the reaction is carried out continuously in a tubular reactor which may take the form of a copper coil provided with exterior cooling means capable of maintaining the desired low polymerization temperature. The mixture of monoolefin and diolefin, and the liquid reaction medium, either as separate entities or as a previously-formed mixture, are continuously introduced into the refrigerated coil. At the point within the coil where the unsaturated reactants and the reaction medium have been thoroughly mixed and/or cooled, for example, to about −75° C., there is introduced a stream of catalyst, e.g., a mixture of boron trifluoride in methane, ethane, propane, or other inert diluent, containing 5 to 50 parts of diluent per part of boron trifluoride. The polymerization reaction is exothermic, and the reaction temperature and reaction rate (and hence also the molecular weight of the product) can readily be controlled by suitably varying the rate of catalyst addition and/or the catalyst concentration. Generally, between about 0.1 and about 3 parts by weight of catalyst are provided per 100 parts by weight of polymerizable unsaturates. The polymerization may be carried to completion, i.e., to point of maximum molecular weight of the product under the particular conditions employed, or it may be stopped at any desired intermediate point by quenching the reaction by the addition of an alcohol, ether or ketone. As stated, the polymerization reaction should be so controlled, either by suitably selecting the reaction temperature, the amount of inert liquid reaction medium present, the identity, concentration and rate of addition of the catalyst, by use of a quenching agent, or by a combination of these means, to stop the reaction at the desired point so as to obtain a polymeric product having an average molecular weight between about 10,000 and about 150,000. Within this range the copolymer products are of high enough molecular weight to be V.I. improves and yet not so high as to have poor shear stability. Preferably, the copolymer will have an average molecular weight of between about 20,000 and about 80,000. The most desirable copolymers contain from about 0.005 to about 0.05, preferably from about 0.01 to about 0.05, part of the diolefin per part of the copolymer. For purposes of convenience as will appear hereinafter, the amounts of diolefin to be employed will be expressed as parts of diolefin per 100 parts of resulting copolymer. On this basis the desired copolymers will be prepared using from about 0.5 to about 5.0 parts of diolefin per 100 parts of copolymer, and preferably from about 1 to about 3 parts of diolefin per 100 parts of copolymer. This is substantially equivalent to expressing the amount of diolefin as parts per 100 parts of the mixture of monoolefin and diolefin fed to the copolymerization reaction and may be determined in this manner.

It is to be pointed out that unless as much as about 0.5 part of diolefin is used per 100 parts of copolymer, the products obtained do not have the ability to impart the desired high dispersancy to lubricating oils. This lack of dispersancy is also observed when monoolefin polymers are used in place of the copolymers of this invention. Moreover, if amounts of diolefin greater than about 5 parts per 100 parts of copolymer are employed, the tendency for the products to form gels is increased to a point such that the products are not generally useful. This point is discussed more fully and the reason for it explained hereinbelow.

Upon completion of the copolymerization reaction, the product is obtained in the form of a viscous solution of the same in the liquid reaction medium. If the copolymer is to be stored for any appreciable period of time before being reacted with a phosphorus sulfide, it is preferably washed several times with water to remove any catalyst and a portion of the solvent is distilled off to strip off traces of water and unpolymerized olefin or diolefin.

The molecular weights of the copolymers were estimated from the viscosities of solutions in diisobutylene according to the method described by Flory, "Molecular Weights and Intrinsic Viscosities of Polyisobutylenes," Paul J. Flory, J. Am. Chem. Soc., 65, 372 (1943), and "Effect of Molecular Structure on Physical Properties of Butyl Rubber," Paul J. Flory, Ind. Eng. Chem., 38, 417 (1946).

PHOSPHORUS SULFIDE

The phosphorus sulfide used to react with the copolymers described above is preferably phosphorus pentasulfide (P_2S_5), although other sulfides, such as P_2S_3, P_3S_4, P_4S_7 and P_4S_{10} may be employed if desired.

The amount of phosphorus sulfide to be used will be between about 0.01 and 0.1, preferably between about 0.03 and about 0.1, part per part of copolymer. This corresponds to between about 1.0 and about 10; preferably between about 3 and about 10 parts of the phosphorus sulfide per 100 parts of the copolymer. In order to avoid separating unreacted phosphorus sulfide from the reaction product, it is preferred to employ only that amount which will react completely with the copolymer, which amount will vary according to the nature of the copolymer and its molecular weight. In any particular case, the optimum proportions of the two reactants can readily be determined by experimentation. However, if an excess of the phosphorus sulfide is employed it can readily be re-

moved from the reaction product by filtration, preferably after first diluting the latter with a solvent such as hexane. Using amounts of the phosphorus sulfide described herein, the total amount employed will generally be substantially completely consumed in the reaction.

The reaction itself may be carried out simply by mixing the two reactants and subjecting the mixture to a temperature between about 90° C. and about 260° C., preferably between about 150° C. and about 200° C., until the reaction is complete and a maximum amount of the phosphorus sulfide has combined with the polymer. Usually the reaction is complete in from about 2 to about 8 hours. During the heating period, oxygen should be excluded from the reaction mixture as by carrying out the reaction under a blanket of an inert gas such as nitrogen. According to an alternative and preferred mode of operation, the reaction is carried out in the presence of an inert liquid reaction medium which is suitably a boiling hydrocarbon and is preferably a mineral oil fraction of such nature that it may be allowed to remain with the reaction product and eventually serve as a diluent for the finished additive as well as a component of lubricating oil compositions comprising such additive. A particularly suitable mineral oil fraction of this nature is the light neutral lubricating fraction having a viscosity of about 38 SSU at 210° F. and a viscosity index of about 84, and customarily referred to as "90 neutral oil."

METAL BASE

The reaction products prepared as described above contain both phosphorus and sulfur in chemically combined form, and show a titratable acidity which can be neutralized with a metal base. Such neutralization can be effected using an alkali or an alkaline earth metal base. The neutralized products are then superbased, i.e., additional base can be incorporated therein in soluble or dispersible form following certain techniques as described later. The additional base must be an alkaline earth metal base. By the term "alkali metal base" is meant the oxide, hydroxide or carbonate of sodium, potassium or lithium. By the term "alkaline earth metal base" is meant the oxide, hydroxide, hydrated oxide or carbonate of calcium, barium or strontium. It will be apparent that one or more of the mentioned metal bases can be used to effect neutralization, and one or more alkaline earth metal bases can be used to effect superbasing. Of the above metal bases, barium oxide, barium hydroxide or the hydrated oxide of barium are preferred.

Preferably, the neutralization and superbasing is effected in one step. The acidic sulfur- and phosphorus-containing polymer produced as above described is reacted with between about 1.5 and about 3.5 chemical equivalents of an alkaline earth metal base. Alternatively, the mentioned acid polymer is neutralized by reaction with the required amount of an alkali or alkaline earth metal base and the neutralized product then superbased by reaction with between about 0.5 and 2.5 chemical equivalents of an alkaline earth metal base.

As previously stated, if it is attempted to combine the sulfur- and phosphorus-containing acidic polymer with an alkaline earth metal base in an amount beyond that required for neutralization, the excess base does not dissolve completely to form a liquid homogeneous product, but instead there is formed a non-uniform sticky gel which is very difficult to handle and is completely unsatisfactory for use as an additive. This difficulty is overcome, however, by carrying out the superbasing or neutralization and superbasing in the presence of required proportions of an alkyl phenol as described herebelow.

ALKYL PHENOL

Alkyl phenols which are useful in effecting the desired solubilization of excess metal base in the additives of this invention are the oil-soluble alkyl phenols having between about 4 and about 10 carbon atoms in the alkyl group or groups. Such phenols may contain one or more alkyl groups and preferably one or two alkyl groups. The preferred phenols are octyl or nonyl phenols. Particularly effective compounds include tert-butyl phenyl, isobutyl cresol, p-octyl phenol, mixed nonyl phenols, mixed dodecyl phenols and dihexyl phenol. Amounts of alkyl phenol to be used vary between 5 parts and 100 parts per 100 parts of the acidic sulfur- and phosphorus-containing copolymer. Unless about 5 parts are used the effect of the alkyl phenol is not generally enough to assist appreciably in effecting superbasing and to use over 100 parts (equal parts of alkyl phenol and acidic copolymer) is generally uneconomical. Moreover, greater amounts of the alkyl phenol are sometimes objectionable in the finished additive.

Preferably both the neutralization and superbasing will be carried out in one step in the presence of the alkyl phenol. According to such preferred mode of operation, the acidic copolymer reaction product is admixed with from about 5 to about 100 parts by weight of one or a mixture of alkyl phenols of the present class, after which the mixture is heated to between about 100° C. and about 180° C., and the desired amount of the desired alkaline earth metal base is added gradually with stirring over a period of 1 to 4 hours.

During neutralization of the acidic reaction product with the metal base at the elevated temperatures stated above, the water which is formed in the neutralization reaction vaporizes from the mixture. It is preferred to replace such water more or less continuously, as by adding water drop-wise to the reaction mixture, or by using a base containing water of crystallization, during the initial part of the heating period. After addition of the metal base the reaction mixture is heated for 1 to 4 additional hours to ensure completion of the neutralization reaction and to evaporate off all the water. The resulting product is then diluted with a petroleum fraction, preferably of light lubricating oil viscosity, and is clarified by filtration to obtain the additive as a 15% to 50% solution in mineral oil, which is the form in which lubricating oil additives are conventionally handled and marketed. Such additive solutions are usually referred to as "additive concentrates."

Although the particular reactants described above employed under the conditions and in the amounts indicated above will generally produce satisfactory additives and additive concentrates, unless additional restrictions are placed on the composition, i.e., on the molecular weight of the copolymer, the amount of phosphorus sulfide and the amount of alkyl phenol, many of the compositions are found to produce additives which gel during the neutralization and superbasing step and are thus unsatisfactory. It has been found that the following equation defines compositions which are useful and which do not gel:

$$\text{Minimum alkyl phenol} = \frac{\text{mol. wt.} \times \text{isoprene} \times \text{phosphorus sulfide}}{10{,}000}$$

where "mol. wt." is the molecular weight of the copolymer; "isoprene" is the parts by weight of isoprene per 100 parts by weight of the copolymer; "phosphorus sulfide" is the parts by weight of phosphorus sulfide per 100 parts by weight of the copolymer; and "alkyl phenol" is the parts by weight of alkyl phenol per 100 parts by weight of the phosphorus sulfide treated copolymer. Thus, the equation shows the minimum amount of alkyl phenol which must be used for a given copolymer-phosphorus sulfide reaction product to prevent gel formation in the additive concentrate during or following neutralization and superbasing.

The amount of superbasing within the limits indicated herein does not appear to influence the values set forth in the above equation. Whether or not gelling occurs and

unsatisfactory additives are obtained depends upon the factors taken into consideration by the above equation.

In applying the equation to an additive prepared from the minimum molecular weight copolymer (10,000), containing the minimum proportion of isoprene (0.5 part per 100 parts of copolymer), and treated with the minimum proportion of P_2S_5 (1 part per 100 parts of copolymer), only 0.5 part of alkyl phenol would be required to prevent gelling. It is pointed out, however, that at least about 5 parts of alkyl phenol are generally required to effect solubilization of the desired excess base. However, in the preferred embodiment of the invention, the isoprene is at least 1 and the P_2S_5 at least 3 for molecular weights of 10,000 to 40,000. For very high molecular weights the preferred isoprene may be 0.5 and the preferred P_2S_5 at least 3. Consequently, in all of the preferred examples the alkyl phenol will be at least 5%. On the other hand, if the calculated value for alkyl phenol is greater than 100, the products cannot be made economically and the combinations of molecular weight, isoprene content and P_2S_5 treatment requiring such an excess of alkyl phenol are not preferred embodiments of the invention.

Application of this equation will be made in the examples set forth herein to show its criticality and its usefulness in selecting reactants, and amounts of reactants to be used in preparing additives of this invention.

While the additive compositions provided by the invention are "all-purpose" in the sense that they impart a high viscosity index and detergent and anticorrosion properties to the base oils with which they are compounded, it is frequently desirable that they be employed in conjunction with the other additives which are conventionally employed to impart special properties to finished lubricating compositions. Thus, they are frequently employed in conjunction with pour point depressants, such as acrylate polymers, (for example, Rohm and Haas Co. "Acryloid 710" and "Acryloid 917"), and with bearing corrosion inhibitors such as the oil-soluble metal salts of the acidic reaction products obtained by reacting phosphorus pentasulfide with an alcohol. A commercially available product of this type, Lubrizol 1060, is a zinc dialkyl dithiophosphate. These latter products are often referred to as organic-substituted thiophosphates. The alcohols employed in the preparation of the thiophosphates include aliphatic alcohols such as butyl, amyl, isoamyl, hexyl, heptyl, octyl, lauryl and cetyl alcohols. These alcohols may be modified by the inclusion of phenyl or other aromatic groups forming alkaryl or aralkyl-substituted alcohols. Also cycloaliphatic alcohols such as cyclopentanol, cyclohexanol, cycloheptanol or alkyl-substituted cycloaliphatic alcohols in which the substituents contain less than about 10 carbon atoms. The method of preparing these thiophosphates is fully described in the Freuler U.S. Patent No. 2,634,284. Metals used to neutralize the acidic reaction products include the alkali metals sodium, potassium and lithium, the alkaline earth metals calcium, strontium, barium and magnesium, and the various heavy metals. Of this latter group zinc is the preferred metal, although tin, antimony, lead, nickel, etc., may be employed in some instances.

The particular thiophosphates which appear to have exceptional bearing corrosion inhibition are the metal dialkyl dithiophosphates in which the alkyl substituents contain a total of between about 8 and about 30 carbon atoms. Of this group the zinc dialkyl dithiophosphates, such as zinc dioctyl dithiophosphate are particularly preferred.

Although it is often desirable to incorporate a metal dialkyl dithiophosphate such as particularly a zinc dialkyl dithiophosphate in lubricating oils containing the additive of this invention, it is found that where such a combination is included in mineral lubricating oil there is often produced small amount of insoluble material which must be filtered from the oil following incorporation of the combination additive. This difficulty is eliminated, however, if the additive of this invention is treated with carbon dioxide prior to being compounded with the thiophosphate. This treatment consists simply in passing a stream of carbon dioxide through the additive or the additive concentrate at a temperature of about 80°–150° C. for from about 1 to about 4 hours. The resulting additive is found to be entirely compatible with the metal thiophosphates described.

In preparing the lubricating oil compositions of the invention, a sufficient amount of the additive, usually in concentrate form, is added to the base oil to impart thereto the desired viscosity index, detergent, dispersant and anticorrosion properties. In general, the finished composition will contain between about 1% and about 10% by weight of the additive, corresponding to between about 3% and about 25% by weight of the above-described additive concentrate. Substantially any mineral oil of lubricating viscosity produced from paraffinic or naphthenic crudes may be employed as the base oil. Because the additives and additive concentrates are easily oil-soluble and/or dispersible it is merely necessary to mix them with base oil at ordinary temperatures to prepare the finished lubricating oil product. In order to hasten the mixing, particularly with the more viscous grades of oil, it may be advantageous in some instances to mix at somewhat elevated temperatures.

Amounts of supplemental additives will generally be in the range of 0.2% to 2% for the metal dialkyl dithiophosphate and between 0.2% to 4% for the pour point depressant. The amount of the latter will depend to a great extent on the amount of additive of this invention which is employed. With larger proportions of the additive of this invention, smaller proportions of Acryloid 710 or Acryloid 917 will be used.

In order to obtain the advantages of the invention to the greatest degree, it is preferred that the base oil be one which has been refined by solvent extraction methods to remove aromatic constituents. Also, it is preferred that the base oil have a viscosity index of 80–85 or higher in order that the finished composition may have a viscosity index of 100 or above without the necessity of employing more than about 10% of the additive. Moreover, the detergent characteristics of the finished composition are usually higher when the base oil is one having a viscosity index above about 80. On the other hand, the additives provided by the invention are very effective in raising the viscosity index of base oils which are of poor quality in this respect, i.e., base oils whose viscosity indexes are of the order of 20 to 70, to that of medium to good quality oils. Similar improvement in the detergent and anticorrosion characteristics of relatively low quality base oils may be obtained through the use of the present additives in only moderate amounts.

Typical oils used in preparing the lubricating oils of this invention are "90 neutral oil" and "300 neutral oil" and mixtures of these oils. These oils have the following characteristics:

	Viscosity, 100° F.	SSU at 210° F.	Viscosity Index
90 Neutral oil	89	38	84
300 Neutral oil	326	52.5	86

Engine tests to determine the detergency and dispersability characteristics of the additives of this invention have been made in standard 1954 Chevrolet "Power-Glide" engines. Tests in these engines have been made for two different periods of time, i.e., for 54 hours and for 96 hours. The engine is operated under varying conditions of load and temperature. Thus, the engine is operated for 2 hours under the conditions set forth in column A of the table below, then for 2 hours under

the conditions set forth in column B, and finally for 2 hours under the conditions set forth in column C. This cycle is repeated nine times in the 54-hour test and sixteen times in the 96-hour test, and at the end of the time indicated the engine is disassembled and inspected for general condition and cleanliness.

TEST CONDITIONS

	A	B	C
Speed, r.p.m.	600	2,500	2,500
Load, lbs.	0	64	64
Brake H.P.	0	40	40
Water Temp.:			
° F. in.		85±5	
° F. out	125±5	95±5	200±5
Oil Temp., ° F	120±5	185±5	200±5

In examining the disassembled engine following completion of the test, the following ratings are given.

Piston rating.—This is the average cleanliness rating of the thrust and antithrust faces of 6 pistons. The rating scale is from 0 to 100 with 100 indicating a perfectly clean surface.

Varnish rating.—In this rating 6 parts of the engine are rated for varnish deposit. These parts are piston skirts, rocker arm cover, push rod cover, cylinder walls and crankcase oil pan. The rating scale is 0 to 100 with 100 indicating complete absence of varnish.

Sludge rating.—Seven parts of the engine are rated on a scale of 0 to 100 with 100 indicating complete absence of sludge. The sludge appears on the surfaces as an oil-wet deposit of appreciable thickness. The engine parts rated are the rocker arm assembly, rocker arm cover, push rod cover, oil screen, crankcase oil pan, push rod chamber and valve top deck.

It will be noted that several of the same engine parts are rated for both varnish and sludge. In these cases, the sludge is first rated, then removed by washing with hydrocarbon solvent, e.g., naphtha, and the varnish is then rated. Both types of deposits are found on these parts.

Another engine test which has been used to evaluate additives of this invention will be referred to as the "Oldsmobile light duty detergency test," or simply the "Oldsmobile test." This is a cyclic test run for 144 hours in a 1956 Oldsmobile V-8 engine under conditions simulating average passenger car service. Engine coolant is controlled at 85° F. for 15% of the time, and at 135° F. for the remainder of the operating period. Engine oil temperature is varied from 115° F. to 145° F. in a manner simulating actual service. The engine speed is continuously cycled from idle to 1700 r.p.m. at a moderate road load. At the end of the test period, the engine is disassembled and rated for piston cleanliness and sludge. In each instance the rating is on a scale of 0 to 100, where 100 indicates a perfectly clean engine. In the sludge rating, the engine parts rated are the same as those described in connection with the Chevrolet test.

The following examples will illustrate several ways in which the additive compositions of the invention have been prepared, but are not to be construed as limiting the invention. All proportions are given in parts by weight unless otherwise indicated.

Example I

The apparatus consists of 18 feet of 0.25-inch copper tubing in the form of a coil mounted in a Dry Ice and acetone bath. The inlet end of the coil is equipped with two fittings through which monomeric olefin and solvent containing diolefin can be introduced into the coil. A second fitting for the introduction of catalyst is positioned about 14 feet from the inlet end of the coil, and the outlet end of the coil feeds into a receiver. Suitable throttling valves, flow meters and associated equipment are provided for controlling the rate at which the olefin, solvent containing diolefin and catalyst are introduced into the coil, and thermocouples are provided for determining the temperature of the reaction mixture within the coil.

In a typical copolymer preparation 400 parts of isobutylene and 1,300 parts of pentane containing 9 parts of isoprene are introduced per hour into the coil. The catalyst consisting of a mixture of one part of boron trifluoride and 20 parts of propane is introduced at a rate of about 1.5 parts per hour. At these flow rates the temperature of the reaction mixture is about —65° C. to —75° C., and the reaction time is about 1.5 minutes. The product collected in the receiver is a pentane solution of about 23% concentration of an isobutylene-isoprene copolymer having an average molecular weight of about 20,000. This solution is concentrated to about 35% by distilling off the required amount of solvent. Approximately 4,000 parts of this copolymer solution (1,400 parts of copolymer) are admixed with 1,400 parts of 90 neutral oil, and the resulting mixture is heated at about 150° C. while blowing with nitrogen to remove the pentane solvent. The resulting product is then admixed with 70 parts (equivalent to 5 parts per 100 parts of copolymer) of phosphorus pentasulfide and the temperature is increased to about 180° C. and held there for about six hours. The product is then filtered and cooled. This product should require at least 22 parts of alkyl phenol to prevent gelation as determined by substituting the above values in the equation set forth herein:

$$\text{Minimum alkyl phenol} = \frac{20{,}000 \times 2.2 \times 5}{10{,}000} = 22$$

A 100-part portion of the phosphorus- and sulfur-containing product so prepared is then heated with stirring at about 130° C. while 17.5 parts of barium hydroxide pentahydrate are added over a period of one hour. Heating is continued for about 4.5 hours, during which time 12.5 parts of water are added to replace that lost by evaporation. During the heating, the product becomes very thick and viscous and tends to climb up the stirrer shaft and stick to the walls of the vessel. Because of these difficulties, it is of non-uniform appearance and composition. Upon completion of the heating period the product is dehydrated by heating to about 165° C., after which it is diluted with 100 parts of 90 neutral oil and is filtered. The filtration operation is rendered difficult by the fact that the product takes the form of a thin gel which clogs the interstices of the filtering medium. The finished product has a base number of only about 5.12.

A second 100-part portion of the phosphorus- and sulfur-containing copolymer is admixed with 25 parts of nonyl phenol, and is then treated with barium hydroxide as described above. Throughout the operation, the reaction mixture remains quite fluid and presents no difficulties in filtration. The finished product has a base number of about 25. When 35 parts of the nonyl phenol are employed, the finished product has a base number of about 26, and if 50 parts of the phenol are employed the base number of the product is about 30. Substantially the same results are obtained when tert-butyl phenol is employed instead of nonyl phenol.

A 54-hour Chevrolet engine test on a lubricating oil containing 4% of the additive prepared by neutralizing with 17.5 parts of barium hydroxide pentahydrate in the presence of 25 parts of nonyl phenol in a neutral oil of SAE 10W grade gives the following results:

Piston rating	95
Varnish rating	91
Sludge rating	83

For comparison, in the same test the base oil gives the

following results after 39 hours when the test was discontinued:

Piston rating	43
Varnish rating	63
Sludge rating	39

For further comparison, a sample of base oil containing 12% of Paratone N was tested in the Chevrolet engine. Paratone N, which is a commercial additive, was added in order to make the viscosity and V.I. of the base oil similar to that of the oil containing additive. The results were as follows:

Piston rating	44
Varnish rating	72
Sludge rating	53

Example II

A copolymer of 97 parts of isobutylene and 3 parts of isoprene is prepared using the conditions set forth in Example I. This copolymer with a molecular weight of about 10,000 is heated to vaporize a portion of the solvent, mixed with 90 neutral oil and further heated to 150° F. to drive off all of the pentane solvent leaving a 35% solution of copolymer in mineral lubricating oil.

To 2,800 parts of the copolymer solution (980 parts of copolymer) is added 70 parts of phosphorus pentasulfide (7.1 parts per 100 parts of copolymer), and the mixture heated to 180° C. for about six hours. The product is filtered and cooled. Substituting the above values in the equation:

$$\text{Minimum alkyl phenol}=\frac{10{,}000\times 3\times 7.1}{10{,}000}=21.3$$

Thus, at least about 21 parts of phenol are required for 100 parts of P_2S_5 treated copolymer or 273 parts of the oil solution.

To 273 parts of the above oil solution is added 40 parts of barium hydroxide pentahydrate and the mixture heated with stirring at 130° C. for one hour. During this heating, water is added at intervals to maintain small amounts of water in the reaction mixture. A total of about 12 parts of water are used. The product is then heated to 165° C. to expel water. At this time and in fact shortly after starting the heating in the presence of barium hydrate, the reaction mixture is in the form of a gel which is not dispersible in oil to produce a satisfactory lubricating oil.

A second 273-part portion of the oil solution of the phosphosulfurized product is treated in the same manner as above, except that 15 parts of nonyl phenol is added to the phosphosulfurized product prior to treatment with barium hydrate. This product also forms a gel and is unsatisfactory.

A third 273-part portion is treated in the same manner except that 25 parts of nonyl phenol are used. In this case, the reaction product remains fluid and does not gel.

Approximately 20 parts of the above concentrate prepared with 25 parts of nonyl phenol is dissolved in 80 parts of 90 neutral oil and the product tested in the Chevrolet test engine for 54 hours with the following results:

Piston rating	90
Varnish rating	85
Sludge rating	80

Example III

Example II is repeated up to the neutralization with barium hydrate using a 98 to 2 copolymer of isobutylene and isoprene having an average molecular weight of 50,000.

According to the equation set forth herein, a minimum of 71 parts of alkyl phenol is required. Neutralization is carried out with 75 parts of barium hydrate and 72 parts of nonyl phenol following the teaching of Example I, except that additional oil was added to give a 25% solution. This product is free of gelation and is readily filterable and dispersible in mineral oil. This concentrate containing about 30% of neutralized copolymer has a base number of about 50.

A lubricating oil containing 10% of this concentrate gives the following results in the 54-hour Chevrolet test:

Piston rating	95
Varnish rating	87
Sludge rating	76

This example, repeated using octyl phenol in place of nonyl phenol, gives substantially similar results.

Sufficient of this latter concentrate is added to 89 V.I. mineral lubricating oil of SAE 10 grade to give an oil containing 6% of the superbased additive. A 54-hour Chevrolet engine test shows the following:

Piston rating	93
Varnish rating	88
Sludge rating	84

Example IV

To 100 parts of a copolymer of 99.5 parts of isobutylene and 0.5 part of isoprene having an average molecular weight of 140,000 is added 100 parts of 90 neutral oil, and the resulting solution is reacted as described in Example I with 5 parts of P_2S_5. This product is further diluted with an additional 200 parts of 90 neutral oil to give a 25% (approximate) concentrate of P_2S_5-copolymer.

According to the equation, a minimum of 35 parts of alkyl phenol is required to prevent gelation during neutralization. Thus

$$\text{Alkyl phenol}=\frac{140{,}000\times 0.5\times 5}{10{,}000}=35$$

Neutralization with 40 parts of barium hydrate per 100 parts of P_2S_5-copolymer (approximately 400 parts of the oil concentrate) in the presence of 25 parts of nonyl phenol results in a very heavy, almost rubbery gel.

Repeating the above with 40 parts of nonyl phenol results in an entirely satisfactory product that is filterable to give a clear, bright, non-gelled concentrate.

A lubricating oil containing 8% of the oil concentrate in a base oil consisting of 25% of 300 neutral oil and 75% of 90 neutral oil gives the following test results in the Chevrolet engine:

Piston rating	92
Varnish rating	87
Sludge rating	81

Example V

To 100 parts of a copolymer of 99 parts of isobutylene and 1 part of isoprene having an average molecular weight of 12,000 is added 100 parts of 90 neutral oil, and the resulting solution reacted with 4 parts of phosphorus pentasulfide per 100 parts of copolymer. The temperature is maintained at about 180° C. for 5 hours and the product is filtered and cooled. According to the equation set forth herein in order to prevent gelation during neutralization at least about 4.8 parts of alkyl phenol are required.

Neutralization and superbasing is carried out using 15 parts of barium hydrate and 5 parts of nonyl phenol per 100 parts of the phosphosulfurized copolymer. Neutralization takes place without gel formation.

A lubricating oil prepared by dissolving 10% of the

above product in an SAE 10 mineral lubricating oil of 84 V.I. gives the following results in a Chevrolet engine test:

Piston rating	89
Varnish rating	86
Sludge rating	81

Example VI

Example V is repeated, except that in place of barium hydrate, calcium hydroxide is employed in substantially equivalent amounts. During the neutralization small amounts of water are added at intervals in order to maintain water in the reaction mixture. After completion of the reaction at about 135° C., the temperature is increased to 165° C. in order to vaporize water from the reaction product.

A lubricating oil prepared by dissolving 8% by weight of the above product in a mineral oil such as employed in Example V gives the following test results:

Piston rating	88
Varnish rating	84
Sludge rating	80

Example VII

To 100 parts of a copolymer of 98 parts of isobutylene and 2 parts of isoprene having an average molecular weight of 40,000 is added 100 parts of 90 neutral oil, and the resulting solution is reacted as described in Example I with 5 parts of P_2S_5. This product is further diluted with sufficient 90 neutral oil to give a concentrate containing 25% by weight of the phosphorus- and sulfur-containing copolymer. The minimum quantity of alkyl phenol necessary to prevent gelation during neutralization calculated from the equation herein is 40.

To 400 parts of the above solution (100 parts of the P_2S_5-copolymer) is added 35 parts of barium hydrate and 50 parts of nonyl phenol, and the reaction mixture is heated and stirred for approximately four hours at 135° C. At the end of this period, the product is filtered. No gelation occurred during its preparation.

A lubricating oil is prepared by dissolving 20 parts of the above concentrate in 100 parts of mineral lubricating oil. This oil gives the following results in the Chevrolet engine test:

Piston rating	94
Varnish rating	86
Sludge rating	83

To another similar portion (20 parts) of the concentrate prepared above is added one part of a commercial zinc dialkyl dithiophosphate which consists of approximately 75% to 80% of the phosphate in mineral lubricating oil and 100 parts of mineral lubricating oil. This particular thiophosphate is obtainable on the market under the designation "Lubrizol 1060." Upon adding the thiophosphate a precipitate occurs in the oil which is difficult to remove by filtration.

A portion of the above oil concentrate of the phosphosulfurized copolymer is diluted with 100 parts of mineral lubricating oil and heated to 130° C. and blown with carbon dioxide for a period of three hours. Following this treatment one part of Lubrizol 1060 is added, and the resulting product is clear with no evidence of insolubility or precipitation of insoluble materials. This product gives the following results in the Chevrolet engine test:

Piston rating	89
Varnish rating	84
Sludge rating	82

Example VIII

The phosphorus- and sulfur-containing copolymer of Example VII is neutralized with strontium hydrate in place of barium hydrate as described in Example VII. Lubricating oils prepared from this oil concentrate before and after blowing with CO_2 as described in the same example, and with and without the presence of Lubrizol 1060, are tested in the Chevrolet engine with the following results:

	Piston Rating	Varnish Rating	Sludge Rating
No CO_2 treatment	95	89	84
Treated with CO_2	94	88	85
Treated with CO_2 and containing 1% of Lubrizol 1060	94	89	83

The presence of the zinc dialkyl dithiophosphate is observed to have little, if any, effect on the detergency or dispersancy of the finished oil.

Example IX

To 100 parts of a copolymer of 98 parts of isobutylene and 2 parts of isoprene and having a molecular weight of 30,000 is added 200 parts of 90 neutral oil and the resulting solution reacted with 7 parts of P_2S_5 under conditions described herein. This product contains approximately 35% by weight of the phosphorus- and sulfur-containing copolymer. From the equation set forth herein, a minimum of 42 parts of alkyl phenol is required to prevent gelation during neutralization and superbasing.

One portion of the above product containing 100 parts of the phosphorus- and sulfur-containing copolymer is neutralized with the theoretical quantity of sodium hydroxide, and then further reacted with 40 parts of barium hydrate after adding 50 parts of nonyl phenol. The product is free from any tendency to gel and when added to mineral lubricating oil in quantities greater than about 2% to 3%, imparts the desired high detergency and high dispersancy characteristics. Also it imparts improved V.I. characteristics.

The foregoing neutralization step is repeated using lithium hydroxide in place of sodium hydroxide. This is followed by treatment with barium hydrate and 50 parts of nonyl phenol as described above. The product is similar in characteristics to the product obtained with sodium hydroxide and lubricating oils prepared therefrom have all of the desired characteristics.

Example X

A 41% pentane solution of a 98 to 2 copolymer of isobutylene and isoprene of 20,000 molecular weight is prepared according to the teaching of Example I. To 3,218 parts of this solution is added 1,270 parts of 90 neutral oil and the pentane is removed by distillation. To this oil solution is added 63.5 parts of P_2S_5, and the mixture is heated at 185° C. for 5 hours. The product is then diluted with an additional 1,270 parts of 90 neutral oil and the product filtered. To 3,659 parts of the above product, containing about 1,280 parts of phosphorus- and sulfur-containing copolymer, is added 1,219 parts of 90 neutral oil, 305 parts of nonyl phenol (24 parts per 100 parts of the P_2S_5-copolymer) and 427 parts of barium hydroxide pentahydrate. The base is added over a period of 1.75 hours at a temperature of 120° C. The product is heated an additional hour at this temperature and then dehydrated at 165° C. and filtered. Following this treatment, carbon dioxide is blown into the product for 2½ hours at 100° C.

A lubricating oil is prepared by dissolving 20% of the above additive concentrate, one part of zinc dioctyl dithiophosphate and 0.9 part of Acryloid 710, a com-

mercial methacrylate polymer, in 53.1 parts of 90 neutral oil and 25.0 parts of 300 neutral oil. This oil has a viscosity at 100° F. of 337 SSU and at 210° F. of 64.3 SSU with a viscosity index of 137.

The Chevrolet engine test run on this oil for a period of 96 hours gives the following results:

Piston rating	76
Varnish rating	86
Sludge rating	61

Example XI

A 97 to 3 copolymer of isobutylene and isoprene having an average molecular weight of 15,000 is prepared following the teaching of Example I. To 3,620 parts of a 31% solution of this copolymer in pentane is added 1,122 parts of 90 neutral oil, the pentane distilled off, and 56.1 parts of P_2S_5 is added. The mixture is heated at 185° C. for 5 hours, diluted with an additional 1,122 parts of 90 neutral oil and filtered. To 3,197 parts of the above concentrate is added 1,066 parts of 90 neutral oil, 266 parts of nonyl phenol and 373 parts of barium hydroxide pentahydrate. The base is added at 120° C. over a period of 1½ hours, and heating is continued for an additional 1 hour, following which the mixture is dehydrated at 165° C. and filtered. The product is blown for two hours with CO_2 at 100° C.

A lubricating oil is prepared from the above additive concentrate by dissolving 20.0 parts of the concentrate, 3.0 parts of Paratone N and 1.0 part of zinc dioctyl dithiophosphate in 51 parts of 90 neutral oil and 25 parts of 300 neutral oil. The resulting oil has Saybolt Universal viscosity at 100° F. of 368 and at 210° F. of 65.3, giving a viscosity index of 132. This product has a base number of 5.64.

In the 96-hour Chevrolet engine test the following results are obtained:

Piston rating	73
Varnish rating	84
Sludge rating	75

Example XII

For purposes of comparison with the additives prepared from copolymers, the following preparation was carried out. Using the apparatus described in Example I, isobutylene and pentane are introduced into the coil at rates of about 400 parts and about 1,300 parts per hour, respectively. The catalyst consisting of a mixture of one part of boron trifluoride and 20 parts of propane is introduced at a rate of about 1.5 parts per hour. The temperature of the reaction mixture is maintained at about −65° C. to −75° C., and the reaction time is about 1.5 minutes. The product collected in the receiver is a pentane solution of about 23% concentration of an isobutylene polymer having an average molecular weight of about 100,000. This solution is concentrated to about 35% by distilling off a portion of the solvent.

Approximately 4,000 parts of the 35% polyisobutylene solution is then diluted with 1,400 parts of 90 neutral oil, and is heated to about 150° C. and blown with nitrogen to remove the pentane solvent. Without reducing the temperature, 70 parts of phosphorus pentasulfide are gradually added to the solvent-free product, and the temperature is increased to about 180° C. and held there for about six hours while blowing with nitrogen. The phosphorus- and sulfur-containing reaction product so obtained is then filtered hot and allowed to cool.

100 parts of the reaction product so obtained is admixed with 10 parts of n-hexyl phenol and is heated with stirring to about 135° C., after which there is then added 17.5 parts of barium hydroxide pentahydrate over a period of about one hour. Heating is continued for about four hours, during which time about 13 parts of water are added to the reaction mixture to replace the water lost by evaporation. The product is then dehydrated by heating to about 165° C., after which it is diluted with about 100 parts of 90 neutral oil and filtered through diatomaceous earth to obtain a finished additive concentrate. This concentrate contains approximately 25% by weight of additive and has a base number of 22.

A lubricating oil containing 18% of the above additive concentrate sufficient to impart an additive concentration of 4.5% of additive is prepared using a solvent-treated and dewaxed Western paraffinic mineral lubricating oil of 89 V.I. Engine tests in the Chevrolet tests engine for 54 hours show:

Piston rating	92
Varnish rating	87
Sludge rating	65

Another 100 parts of the phosphosulfurized product is neutralized with the equivalent amount of barium hydroxide in the absence of phenol. After neutralizing the product is heated to 165° C. to remove water, diluted with 90 parts of 90 neutral oil and filtered to obtain a finished additive concentrate.

A lubricating oil is prepared by incorporating 12% of the additive concentrate in solvent treated and dewaxed Western paraffinic mineral lubricating oil. The finished oil, which has a viscosity at 100° F. of 304 SSU, 65.5 SSU at 210° F., and a V.I. of 146, shows the following test results in the Chevrolet engine:

Piston rating	90
Varnish rating	84
Sludge rating	63

It will be observed that tests on the two oils described in this example show that piston and varnish ratings are similar to the ratings obtained with oils containing the additives of this invention, but sludge ratings are far lower, i.e., 65 and 63, respectively.

Example XIII

For purposes of comparison, the two lubricating oils described in Example XII are run in the Chevrolet test engine for 96 hours. These oils contained isobutylene polymer reacted with P_2S_5 and then neutralized with and without the use of phenol. The oil containing the reaction product neutralized in the presence of phenol shows the following:

Piston rating	72
Varnish rating	80
Sludge rating	34

The oil containing additive neutralized in the absence of phenol shows the following:

Piston rating	70
Varnish rating	76
Sludge rating	28

Example XIV

A series of copolymers prepared following the teaching herein are treated with P_2S_5 and neutralized using barium hydrate and nonyl phenol. In each case sufficient mineral lubricating oil is added to produce an additive concentrate containing 25% by weight of the additive. The mineral lubricating oil consisted of 90 neutral oil. In each case the additive concentrate is blown with CO_2 for two hours at 100° C.

Data with respect to the molecular weight and isoprene content of the copolymer, the amounts of P_2S_5 and barium hydrate employed, the calculated amount of nonyl phenol required to prevent gelation and whether or not

gel formation occurred is presented in the following tabulation:

TABLE 1

Additive Concentrate No.	Copolymer		P_2S_5, percent	Nonyl Phenol, percent	Barium Hydrate, percent	Calculated Nonyl Phenol Required, [a] percent	Gel Formation
	Molecular Wt.	Isoprene, percent					
1	20,000	2	5	25	35	20	No.
2	50,000	1	5	25	35	25	No.
3	60,000	1	5	25	35	30	Yes.
4	35,000	1.5	5	25	35	26	Slight.
5	60,000	1	5	75	75	30	No.
6	60,000	1	10	100	100	60	No.
7	50,000	1	10	50	70	50	No.
8	50,000	1	10	40	70	50	Yes.
9	130,000	1	5	75	75	65	No.

[a] These calculations are made using the equation:

$$\text{Minimum alkyl phenol} = \frac{\text{mol. wt. isoprene} \times P_2S_5}{10{,}000}$$

Lubricating oils are prepared from some of the additive concentrates described above and the resulting oils tested in the Oldsmobile light duty detergency test. The lubricating oil employed in preparing the finished oil is a mixture of 90 neutral oil and 300 neutral oil in such proportions that the finished oil, containing additive concentrate, contains one part of 90 neutral oil to three parts of 300 neutral oil. Supplemental additives are added to many of the oils; however the effect of these additives alone are also determined for purposes of comparison.

Data concerning the amount and number of the additive concentrate used; the base number of the finished oil; the amounts and proportions of supplemental additives; and the results of the Oldsmobile engine tests, are presented in the following tabulation:

TABLE 2

Lubricating Oil, No.	Additive		Base No., MgKOH/g.	Supplemental Additives			Oldsmobile Engine Test Results	
	No.[a]	Percent by wt.		Lubrizol 1060,[b] percent by wt.	Acryloid [c]		Piston Rating	Sludge Rating
					Percent by wt.	No.		
1				0.5	0.9	710	39	42
2 [d]				1.0	5.8	917	79	54
3	1	20	4.6	0.5	0.9	710	88	91
4	2	12	2.4	0.5	0.9	710	82	83
5	4	12	2.8	0.5	0.9	710	82	75
6	7	6.0	2.6	1.0	3.0	917	89	81
7	9	10	5.2	1.0			92	73

[a] See Table 1 for additive description.
[b] A commercial zinc dialkyl dithiophosphate.
[c] Acryloid 710 and 917 are described hereinabove.
[d] Base oil contained 19% 90 neutral, 60% 300 neutral, and 21% 150 Bright Stock.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the methods or materials employed, provided the compositions stated by any of the following claims, or the equivalent of such stated compositions, be obtained.

In the following claims, "parts" in all cases is to be interpreted as meaning parts by weight.

We claim:

1. A lubricating oil additive composition adapted to be diluted with mineral lubricating oil to produce a lubricating oil composition having high viscosity index, detergent, dispersant and anticorrosion characteristics, said additive composition consisting essentially of mineral lubricating oil containing between about 15% and about 50% by weight of a product prepared by (1) reacting 100 parts of an isobutylene-isoprene copolymer having an average molecular weight between about 10,000 and about 150,000 and containing between about 0.5 and about 5 parts of isoprene per 100 parts of copolymer, with between about 1 part and about 10 parts of a phosphorus sulfide at a temperature between about 90° C. and about 260° C. to obtain an acidic phosphorus- and sulfur-containing product; (2) further reacting said acidic product with between about 1.5 and about 3.5 chemical equivalents of an alkaline earth metal base in the presence of between about 5 and about 100 parts of an alkyl phenol containing between about 4 and about 10 alkyl carbon atoms per 100 parts of said acidic product, the amount of said alkyl phenol being at least that amount represented by the equation:

$$\text{Minimum alkyl phenol} = \frac{\text{mol. wt.} \times \text{isoprene} \times \text{phosphorus sulfide}}{10{,}000}$$

where "alkyl phenol" is expressed in parts per 100 parts of said acidic product, "mol. wt." is the average molecular weight of the copolymer, "isoprene" represents the parts of isoprene per 100 parts of copolymer, and "phosphorus sulfide" represents parts of phosphorus sulfide per 100 parts of copolymer.

2. A lubricating oil additive composition according to claim 1 in which said isobutylene-isoprene copolymer has an average molecular weight of between 20,000 and 80,000.

3. A lubricating oil additive composition according to claim 1 in which the metal of said alkaline earth metal base is barium.

4. A lubricating oil additive composition according to claim 1 in which said phosphorus sulfide is phosphorus pentasulfide.

5. A lubricating oil additive composition adapted to be diluted with mineral lubricating oil to produce a lubricating oil composition having high viscosity index, detergent, dispersant and anticorrosion characteristics, said additive composition consisting essentially of a mineral lubricating oil containing between about 15% and about 50% by weight of a product prepared by reacting an alkaline earth metal base with a neutralized phosphorus- and sulfur-containing reacting product, said neutralized reaction product having been neutralized with a metal

base selected from the class consisting of alkali and alkaline earth metal bases, said reaction product being obtained by reacting, at a temperature between about 90° C. and about 260° C., between about 0.01 and 0.1 part of a phosphorus sulfide with 1.0 part of an isobutylene-isoprene copolymer containing between about 0.5 and about 5 parts of isoprene per 100 parts of copolymer, said copolymer having an average molecular weight between about 10,000 and about 150,000, said reaction product being characterized by ability to enhance the viscosity index, detergent and dispersant characteristics of mineral lubricating oils, and the said reaction between said alkaline earth metal base and said neutralized phosphorus- and sulfur-containing reaction product being effected in the presence of between about 5 parts and about 100 parts, per 100 parts of copolymer-phosphorus sulfide reaction product, of an oil-soluble alkyl phenol containing from 4 to 10 side-chain carbon atoms and with between about 0.5 and about 2.5 acid equivalents of said base being provided per acid equivalent of said reaction product, said amount of alkyl phenol, expressed in parts per 100 parts of the copolymer-phosphorus sulfide reaction product, being at least that amount represented by the equation:

$$\text{Minimum alkyl phenol} = \frac{\text{mol. wt.} \times \text{isoprene} \times \text{phosphorus sulfide}}{10{,}000}$$

where "mol. wt." is the average molecular weight of the copolymer, "isoprene" represents the parts of isoprene per 100 parts of copolymer, and "phosphorus sulfide" represents the parts of phosphorus sulfide per 100 parts of the copolymer.

6. A lubricating oil additive composition adapted to be diluted with mineral lubricating oil to produce a lubricating oil composition having high viscosity index, detergent, dispersant and anticorrosion characteristics, said additive composition consisting essentially of mineral lubricating oil containing between about 15% and about 50% by weight of a product prepared by (1) reacting, at a temperature between about 90° C. and about 260° C. 100 parts of an isobutylene-isoprene copolymer having an average molecular weight between about 10,000 and about 150,000 and containing between about 0.5 and about 5 parts of isoprene per 100 parts of copolymer, with between about 1 part and about 10 parts of a phosphorus sulfide to obtain an acidic phosphorus- and sulfur-containing product; (2) further reacting said acidic product with between about 1.5 and about 3.5 chemical equivalents of an alkaline earth metal base in the presence of between about 5 and about 100 parts of an alkyl phenol containing between about 4 and about 10 alkyl carbon atoms per 100 parts of said acidic product, the amount of said alkyl phenol being at least that amount represented by the equation:

$$\text{Minimum alkyl phenol} = \frac{\text{mol. wt.} \times \text{isoprene} \times \text{phosphorus sulfide}}{10{,}000}$$

where "alkyl phenol" is expressed in parts per 100 parts of said acidic product, "mol. wt." is the average molecular weight of the copolymer, "isoprene" represents the parts of isoprene per 100 parts of copolymer, and "phosphorus sulfide" represents parts of phosphorus sulfide per 100 parts of copolymer; and (3) blowing carbon dioxide through the product of step (2) for a period of about one to about four hours at a temperature of about 80° C. to about 150° C.

7. A lubricating oil additive composition adapted for addition to mineral lubricating oil to produce a lubricating oil composition having high viscosity index, detergent, dispersant and anticorrosion characteristics, said additive composition consisting essentially of a product prepared by (1) dissolving in a mineral lubricating oil an acidic phosphorus- and sulfur-containing product obtained by reacting an isobutylene-isoprene copolymer containing between about 0.5 and 5 parts of isoprene per 100 parts of copolymer, said copolymer having an average molecular weight between about 10,000 and about 150,000, with between about 1 and about 10 parts of phosphorus pentasulfide per 100 parts of copolymer, at a temperature between about 90° C. and about 260° C., said phosphorus- and sulfur-containing product when neutralized being characterized by its ability to enhance the viscosity index, detergent and dispersant characteristics of mineral lubricating oils; (2) adding to the solution so obtained between about 5 and about 100 parts per 100 parts of said phosphorus- and sulfur-containing product contained therein, of an oil-soluble alkyl phenol containing from 4 to 10 side-chain carbon atoms; (3) heating the resulting composition with between about 1.5 and about 3.5 acid equivalents of barium hydroxide pentahydrate per acid equivalent of said phosphorus- and sulfur-containing product present, said heating being effected at a temperature between about 100° C. and about 180° C. over a period from about 2 to about 8 hours; (4) treating the resulting product with carbon dioxide at such temperataure and for such length of time that substantially no precipitate forms upon admixing the treated product with a metal dialkyl dithiophosphate; and (5) diluting the product so obtained with sufficient mineral lubricating oil to obtain a composition containing between about 15% and about 50% by weight of the neutralized phosphorus- and sulfur-containing product; the amount of alkyl phenol added in step (2) being at least that amount represented by the equation:

$$\text{Minimum alkyl phenol} = \frac{\text{mol. wt.} \times \text{isoprene} \times P_2S_5}{10{,}000}$$

where "alkyl phenol" is expressed in parts per 100 parts of copolymer-P_2S_5 reaction product, "mol. wt." represents the average molecular weight of the copolymer, "isoprene" represents the parts of isoprene per part of copolymer, and "P_2S_5" represents the parts of phosphorus sulfide per 100 parts of copolymer.

8. A lubricating oil composition consisting essentially of a mineral lubricating oil having dissolved therein sufficient of a composition of claim 1 to enhance substantially the viscosity index, detergent, dispersant and anticorrosion characteristics of said oil.

9. A lubricating oil composition consisting essentially of a mineral lubricating oil having dissolved therein sufficient of a composition of claim 2 to enhance substantially the viscosity index, detergent, dispersant and anticorrosion characteristic of said oil.

10. A lubricating oil composition consisting essentially of a mineral lubricating oil having dissolved therein sufficient of a composition of claim 3 to enhance substantially the viscosity index, detergent, dispersant and anticorrosion characterstics of said oil.

11. A lubricating oil composition consisting essentially of a mineral lubricating oil having dissolved therein sufficient of a composition of claim 6 to enhance substantially the viscosity index, detergent, dispersant and anticorrosion characteristics of said oil.

12. A lubricating oil composition consisting essentially of a mineral lubricating oil having dissolved therein sufficient of a composition of claim 7 to enhance substantially the viscosity index, detergent, dispersant and anticorrosion characteristics of said oil.

13. A lubricating oil composition consisting essentially

of a mineral lubricating oil having dissolved therein sufficient of a composition of claim 6 to enhance substantially the viscosity index, detergent, dispersant and anticorrosion characteristics of said oil, and between 0.2% and 2% by weight of zinc dialkyl dithiophosphate.

14. A lubricating oil composition consisting essentially of a mineral lubricating oil having dissolved therein sufficient of a composition of claim 7 to enhance substantially the viscosity index, detergent, dispersant and anticorrosion

characteristics of said oil, and between 0.2% and 2% by weight of zinc dialkyl dithiophosphate.

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