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# LUBRICANT COMPOSITIONS

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This invention relates to lubricating oil mixtures containing additives which inhibit sludge formation.

The lubricants of internal combustion engines are particularly subjected to deterioration at the moving surfaces and by the products of combustion coming in contact with the lubricant. These deleterious effects of temperature and hot gases, some of which contain sulphur bodies, cause slow oxidative degeneration of the oil and eventually results in sludge formation. The sludge initially formed frequently remains in the oil suspension but eventually sludge is deposited throughout the engine.

The sludge held in an oil suspension functions satisfactorily as a lubricant and some authorities consider that the sludge when in suspension imparts beneficial properties to the oil. Conversely sludge deposition in the engine is to be avoided. For example, deposited sludge on hot pistons results in a varnish and carbon formation which eventually results in ring sticking. Excessive sludge deposition in cooler parts of the engine can interfere with pressure oil lubrication and lead to a breakdown of the lubrication system.

Numerous efforts have been made to discover lubricating oil additives which can inhibit sludge deposition. Metal soaps and salts are one well-known class of sludge inhibitors. Unfortunately these sludge inhibitors have the great disadvantage that they can deposit oil insoluble material in the crank case and oil pump and deposit ash in the hot regions of the engine. This ash which collects in the combustion chamber leads to premature ignition, damage to the sparking plugs, burning out of the valves and excessive cylinder wear.

In order to overcome the disadvantages associated with ash-forming additives, research has been directed towards the production of additives which contain no inorganic elements. The applicants investigated the preparation and detergent properties of certain oil-soluble copolymers.

As in the field of chemotherapy the research worker in the field of ashless detergents is not aided in his investigation by established theories and hypotheses. It will therefore be appreciated that the discovery of a new polymeric additive can only be derived after detailed research much of which is of an empirical nature. The discovery made by the applicants is an example of (1) the empirical nature of research in the field of ashless detergents, (2) the difficulty of predicting the detergent properties of a polymer and (3) the unexpected nature in which improvements in this field are discovered.

The applicants made the unexpected discovery that considerable increase in sludge dispersancy was obtained by including in a lubricant two different polymeric additives. These two polymeric additives and the synergism resulting from their combined use are discussed later in this specification.

This application is a continuation-in-part of Serial No. 619,126 "Improvements to Lubricant Compositions" filed October 30, 1956, and now abandoned and of Serial No. 561,676, "Lubricating Oil Additive" filed January 26, 1956, by the present inventors.

In brief compass this invention proposes a lubricating oil containing in the range of 0.005 to 6 wt. percent of a stabilized phosphosulphurized polymerised olefin having a Staudinger molecular weight in the range of 3,000 to 5,000



and in the range of 0.004 to 9.5 wt. percent of a polymerised alkoxy ester having a Staudinger molecular weight in the range of 3,000 to 50,000.

The stabilised phosphosulphurised polymerised olefin is obtained by reacting at a temperature within the range of 300 to 550° F. a polymerised olefin, having a Staudinger molecular weight in the range of 900 to 1,600 and obtained from a mono-olefin having 3 to 5 carbon atoms per molecule, with 5 to 30 wt. percent of a sulphide of phosphorus until in the range of 2 to 12 wt. percent of sulphur and 1 to 7 wt. percent of phosphorus are incorporated therein. This phosphorus and sulphur-containing product is then reacted with an alkylene oxide having in the range of 2 to 3 carbon atoms per molecule at a temperature in the range of 176° F. to 302° F. and for a time in the range of 2 to 10 hours until on the average 1 to 10 alkylene oxide residues are included in the stabilised phosphosulphurised polymerised olefin product.

The polymerised alkoxy ester is obtained by reacting a partial ester mixture of maleic acid and an aliphatic monohydric alcohol, containing in the range 3 to 20 carbon atoms per molecule, with an alkylene oxide having in the range of 2 to 3 carbon atoms per molecule at a temperature in the range of 176° F. to 302° F. for a time in the range of 0.5 to 2 hours to obtain an alkoxy ester having on the average of 1 to 10 alkylene oxide residues per mole of alkoxy ester and polymerising the alkoxy ester so obtained at a temperature in the range of 140° F. to 212° F. and in the presence of a polymerisation catalyst.

In a preferred embodiment, the alkoxy ester intermediate product is copolymerised with 15 to 30 wt. percent of a vinyl ester having in the range of 4 to 20 carbon atoms per molecule. In a particularly preferred embodiment the polymerisation of the alkoxy ester is carried out not only in the presence of a vinyl ester but also in the presence of further amounts of an ester of maleic acid.

Further description of the stabilised phosphosulphurised polymerised olefin will now be included.

The technique of polymerising mono-olefins is not described in detail in this specification since this technique is well-known in the art and the present invention involves the use of products derived from the polymerised olefins. The term polyolefin is often used in the art for the term polymerised olefin as used herein. For example polymerised isobutylene is referred to as polybutene.

The polymerised olefins may be prepared by polymerising a mono-olefin, containing from 3 to 5 carbon atoms, preferably under the influence of a Friedel-Crafts catalyst. It is possible to polymerise $C_3$ to $C_5$ olefins by means of boron trifluoride catalyst to give a wide molecular weight range of polymers. For the purposes of the present invention low molecular weight polymerised olefins are preferred e.g. those with a molecular weight range of 900 to 1,600. The most useful polymerised olefin is that homopolymer derived from isobutylene and referred to as polybutene.

In general the applicants have noted, the higher molecular weight of the polymerised olefin, the less effective is the product. It would appear that among the active elements of the stabilized phosphosulphurised polymerised olefin are the atoms of sulphur and phosphorus and alkoxy groups. Unfortunately it has been discovered there is a minimum molecular weight of polymerised olefin that may be phosphosulphurised to give an additive possessing sufficient detergency. Polymerised olefins with molecular weights below about 900 do not give phosphosulphurised products of use in the compositions of the present invention.

The applicants have shown that phosphosulphurised Bright stock or phosphosulphurised synthetic rubber such as butyl rubber, may be used in place of the polymerised olefin. The synthetic rubber may be suitably degraded to

be within the required molecular weight range referred to above. The compositions based on phosphosulphurised rubber or Bright stock are not as effective at equivalent concentrations as those based on the aforementioned polybutenes. However, it may be desirable to use these slightly less effective additives when considerations of cost and availability of starting materials become important factors.

The phosphorus sulphide may be made by interaction of elemental sulphur and phosphorus, dissolved in a solvent if necessary. A mixture of phosphorus sulphide may thereby be obtained. The polybutene may be used as the solvent for preparing the phosphorus sulphide. The preferred phosphorus sulphide for the phosphosulphurisation reaction is phosphorus pentasulphide.

The phosphosulphurisation reaction may be carried out within the temperature range of 194° F. to 608° F. but is preferably carried out within the range of 300 to 550° F. It is preferred to interact 2 to 5 moles of the polymerised olefin with 1 mol of the phosphorus sulphide and to blanket the reaction mixture under an inert gas such as nitrogen. It has been found that $C_3$ to $C_5$ polymerised olefins with a molecular weight within the range of 900 to 1,600 Staudinger molecular weight react with phosphorus pentasulphide at convenient rates at about 300° F. It is therefore desirable to initiate the reaction by slowly heating the polymerised olefin and phosphorus pentasulphide to 300° F. When the initial reaction has subsided the reaction temperature may be slowly raised up to a suitable maximum of 550° F. By this means and with sufficient stirring the reaction may be substantially complete within 2 to 10 hours. It is then advisable to filter this phosphosulphurised product, for example through an activated earth such as kieselguhr, before proceeding to the ethylene oxide reaction stage. In order to increase the stability of the product it is advisable before filtration, or centrifugal separation, to add kieselguhr to the phosphosulphurised product and heat to about 200° F. to 260° F. and blow in carbon dioxide for about half an hour. By this process a phosphosulphurised product should be produced which contains from 2 to 12% of sulphur and from 1 to 7% of phosphorus. The molecular weight of the original polymerised olefin is preferably about doubled or trebled during this process.

The phosphosulphurised polymerised olefin is stabilised by interaction with an alkylene oxide containing from 2 to 6 carbon atoms. However, since alkylene oxides above 4 carbon atoms are not readily available it is preferable to stabilise the phosphosulphurised polymerised olefin with ethylene oxide or propylene oxide. The amount of alkylene oxide that reacts depends on the reaction conditions. It has been found that about 1 molecule of alkylene oxide may be fixed per 1 active hydrogen atom of the phosphosulphurised material by mixing 1 wt. percent of powdered dried caustic soda with the phosphosulphurised polymerised olefin heated at 140° C. and introducing the alkylene oxide e.g. ethylene oxide, into the hot phosphosulphurised mixture. By the use of caustic soda it is not possible without using severe reaction conditions to react more alkylene oxide with the phosphosulphurised product. In order to fix a greater quantity of alkylene oxide it is necessary to use a boron trifluoride ether complex as catalyst. This boron trifluoride catalyst may be conveniently added after the caustic soda initiated reaction is complete. The quantity of boron trifluoride ether catalyst should be about 0.5 to 1% by weight of the phosphosulphurised polymerised olefin, and by using this catalyst from 2 to 10 moles of alkylene oxide may be fixed per active hydrogen atom of phosphosulphurised polymerised olefin.

In order to illustrate the method of preparing the stabilised phosphosulphurised polymerised olefin the following examples are included:

*Example A1.*—A Bright stock having a viscosity of 31.8 cs. at 210° F. and a viscosity index of 98 was mixed and stirred with 10% by weight of phosphorus pentasulphide and gradually heated to 430° F. The reaction was carried out at this temperature for 8 hours under a blanket of nitrogen. The filtrate gave the following analysis: 2.4% P; 4.2% S; acid No. 27.

*Example A2.*—10% by weight of ethylene oxide was absorbed in the filtered product of Example A1 at 285° F. The reaction was carried out over a period of 8 hours. The product gave the following analysis: 2.1% P; 3.6% S; acid No. 0.

*Example B1.*—The product of Example A1 before filtration was mixed with Kieselguhr at 230 to 250° F. and carbon dioxide gas was injected at this temperature over a period of 30 minutes. The filtrate gave the following analysis: 2.2% P; 3.8% S; acid No. 25.

*Example B2.*—10% by weight of ethylene oxide was absorbed in the filtered product of Example B1 at 280° F. The reaction was carried out for a period of 8 hours. The product gave the following analysis: 1.9% P; 2.4% S; acid No. 0.

*Example C1.*—Oronite 32 and 15% by weight of phosphorus pentasulphide were gradually heated to 430° F. and maintained at this temperature for 8 hours under a nitrogen blanket. Oronite 32 is a polybutene i.e. homopolymer of isobutylene, and has a Staudinger molecular weight of 1,200. The product was filtered and gave the following analysis: 3.5% P; 6% S; acid No. 20.

*Example C2.*—6% by weight of ethylene oxide was absorbed in the filtered product of Example C1 at 285° F. The reaction was carried out for a period of 8 hours. The product gave the following analysis: 3.2% P; 5.1% S; acid No. 0.

The stability of the products of the above examples was tested as follows:

800 cc. of a mineral oil of viscosity 14.2 cs. at 210° F. containing 6% by weight of the product of the example under test were placed in a stoppered 1 litre bottle. The bottle was heated at 100° F. for 1 hour and then unstoppered to smell the hydrogen sulphide liberated.

The results were as follows:

| Product of Example | A1 | A2 | B1 | B2 | C1 | C2 |
|---|---|---|---|---|---|---|
| Odour of $H_2S$ | Strong | Nil | Strong | Nil | Strong | Nil. |

These results indicate that the condensation products with ethylene oxide are considerably more stable. It is emphasized that the lubricants of this invention include phosphosulphurised polymerised olefins that have been stabilised by reaction with ethylene oxide.

The anti-oxidising properties were investigated in the following tests carried out on a lubricating oil of viscosity 86 centistokes at 100° F. and viscosity index at 105 containing 1% by weight of the product of the example under test.

200 cc. of the lubricating composition was placed in a 400 cc. beaker. The test was conducted at 320° F. with stirring. Into the lubricating composition were placed a lead and a copper plate, the two plates being changed every 3 hours. Corrosion was measured by the sum of the decreases in the weight of the lead plates after 12 hours. The acid number was measured after 18 hours of this test.

These tests yielded the following results:

| Example | Corrosion, mg. | Acid Number | |
|---|---|---|---|
| | | At Start | After 18 hours |
| Pure oil | 450 | 0.05 | 18 |
| A1 | 2.8 | 0.3 | 0.5 |
| A2 | 0.7 | 0.1 | 0.25 |
| B1 | 2.8 | 0.2 | 0.4 |
| B2 | 1.4 | 0.1 | 0.3 |
| C1 | 2.1 | 0.3 | 0.9 |
| C2 | 0.9 | 0.1 | 0.2 |

The test results show that the stabilised phosphosulphurised polymerised olefin constituent of the lubricants of this invention will not cause a bad odour or excessive corrosion.

After completion of the ethylene oxide reaction and before the product has cooled it is advisable to cut back with a paraffinic lubricating oil. This oil solution may be water-washed and filtered. By this cutting back with a lubricating oil any difficulty associated with dissolving the product in the lubricant is avoided.

Further description of the polymerised alkoxy ester will now be included.

The partial ester mixture of maleic esters may be prepared by esterifying 1 mol of the monohydric alcohol, preferably an aliphatic alcohol containing 3 to 20 carbon atoms in the molecule, with 2 to 4 molecules of fumaric acid, maleic acid or maleic anhydride. From this esterification process a mixture will be obtained which will comprise some diesters of maleic acid, half-esters of maleic acid and any unesterified acid. This mixture of the maleic half-ester is referred to herein as the partial ester mixture.

It has been found to be an advantage to use the half-ester of maleic acid for the preparation of this additive. This half-ester is most conveniently prepared by the interaction of maleic anhydride and the monohydric alcohol by the following method. 1 mole of the aliphatic monohydric alcohol is gradually mixed over a period of 1 hour with molten maleic anhydride (1 mole) maintained at a temperature between 140° F. and 194° F. The reactants molten maleic anhydride (1 mole) maintained at a temperature between 140° F. and 194° F. The reactants are stirred and mixed in a molten state for 1 further half-hour in order to complete the reaction. It has also been found advantageous to prepare the partial ester mixture by esterifying 1 mol of maleic acid within the range of 1.4 to 1.8 mols of the alcohol in the presence of an esterification catalyst. The proportion of the reactants may be adjusted so that the partial ester mixture has an acid number in the range of 30 to 50. Before proceeding with the next stage in the preparation the partial ester mixture may be washed with water to remove esterification catalyst and the washed product so obtained may be dried and reacted with the alkylene oxide without purification.

The alcohols used to prepare the partial ester mixture contain from 3 to 20 carbon atoms per molecule. The particularly preferred aliphatic alcohol components of the esters contain 9 to 10 carbon atoms. The preferred alcohols are straight chain alcohols since it has been shown that the secondary hydrogen atoms of branched chain esters are centres at which oxidation occurs. Accordingly the additives derived from straight chain alcohols have greater stability. However, Oxo alcohols e.g. $C_8$ to $C_{13}$, are not necessarily excluded from the present invention. The preferred straight chain alcohols are normal lauryl, normal octyl, normal decyl and cetostearyl alcohols.

Fumaric or maleic partial esters may be used. Maleic esters are preferred since these esters more readily undergo polymerisation reactions. The interaction of the partial ester and ethylene oxide may be carried out in the same manner as described in preparation of the stabilised phosphosulphurised polymerised olefin type of additive. Again it is preferable to use ethylene oxide and to use proportions of this oxide such that from 1 to 10 mols of ethylene oxide units exist in the polymerised alkoxy ester.

The alkylene oxide derivative of the partial ester mixture may be homopolymerised or copolymerised with another monomer providing that the molecular weight of the homopolymer of this copolymerised alkoxy ester so obtained has a Staudinger molecular weight within the range of 3,000 to 15,000. Vinyl esters are the preferred monomers that may be copolymerised with the polymerised alkoxy ester. The preferred vinyl esters are vinyl acetate and the vinyl esters of $C_8$ to $C_{18}$ fatty acids. It is preferred that these vinyl esters are the esters of saturated straight chain acids but it is possible to use vinyl oleate as the monomer.

The copolymers or homopolymers of the alkoxy ester may be prepared as follows. The partial ester mixture or a mixture of the partial ester mixture and the vinyl ester is mixed with a peroxide catalyst such as benzoyl peroxide or tertiary butyl perbenzoate. The reactants and catalyst are stirred and heated to a temperature in the range of 140° F. to 185° F. The reaction is carried out until viscosity determinations indicate that the desired molecular weight range is obtained. As the reaction proceeds the reaction product increases in viscosity and it is desirable to cut back the reaction mixture with a paraffinic lubricating oil. Without the addition of this lubricating oil sufficient stirring of the mixture becomes difficult and local temperature increases occur. The addition of this oil during the reaction has the further advantage that the product is obtained as an oil concentrate which may then be conveniently blended into the lubricant. The reaction may be quenched by the addition of further paraffinic oil. The amount of oil added during the reaction may be within the range of 10 to 60% by volume of the original volume of the reactants. The amounts of vinyl ester that may be included in the mixture of the partial ester mixture and the vinyl ester should be 1 mol of vinyl ester per 6 to 11 mols of maleic acid residue in the partial ester mixture. When vinyl acetate is the monomer copolymerised with the alkoxy ester it is preferable that the amount of vinyl acetate monomer is in the range of 15 to 30% by weight of the partial ester mixture.

In order to obtain copolymers of the partial ester mixture and vinyl acetate that have high oil solubilities it is preferable to carry out the previously described copolymerisation of the partial ester mixture and vinyl acetate, in the presence of a higher ester of maleic acid. The suitable higher esters of maleic acid used for this purpose are derived from $C_{16}$ to $C_{20}$ alcohols of which the $C_{16}$ to $C_{17}$ Oxo alcohols are particularly preferred.

The following example will serve to explain the process of preparing the polymerised alkoxy ester additive. Maleic acid (1 mol) was esterified with $C_9$ Oxo alcohol (1.6 mol) in the presence of 1% paratoluene sulphonic acid as catalyst. After completion of the esterification reaction the product was washed with water and the non-distilled ester product had an acid number of 40. A stream of ethylene oxide was introduced into this ester at 140° C. along with about 0.5 wt. percent of boron trifluoride as a complex compound with phenol. The quantity of ethylene oxide absorbed by the reactants was 8% and the reaction was carried out over 16 hours, The product obtained i.e. ethoxylated ester, had an acid number of 6. The ethoxylated ester was mixed with 25% by weight of vinyl acetate and 1% by weight of benzoyl peroxide. Copolymerisation was effected at 158° F. for a period of 1 hour. The product was dissolved in a paraffinic lubricating oil to give a concentrated solution of the polymer.

In the preparation of both the polymerised alkoxy ester and the stabilised phosphosulphurised polymerised olefin additives an oil solution of the polymer is obtained. The final stage in preparing the lubricant composition of the present invention is the blending of these two additive concentrates, which should be blended such that the combined polymer concentrate contains in the range of 5 to 60 wt. percent and in particular 10 to 30 wt. percent of the stabilised phosphosulphurised polymerised olefin and in the range of 95 to 40% and in particular 70 to 90% by weight of the polymer or copolymer of the alkoxy ester. The concentrate blend, comprising the two polymers, is dark in colour and has a faint sulphurous odour. The concentrate is viscous but may be readily

dispersed in mineral lubricating oils. The detergent additive of this invention may be used as a dispersant additive in mineral lubricating oils and particularly the lubricating oils to lubricate internal combustion engines.

This combined polymer concentrate may then be diluted with lubricating oil to give the desired lubricant composition and it is preferred that the final lubricant composition contains from 0.1 to 10% of this concentrate. A suitable lubricating oil used for cutting back the polymerisation process used to prepare the polymers and for making the additive concentrate and final lubricant blend, is a paraffinic mineral lubricating oil with a viscosity within the range of 2 to 7 cs. at 210° F. or 27 to 40 cs. at 100° F. It is preferred that this lubricating oil is a distillate oil which has been solvent-treated e.g. phenol-extracted and dewaxed e.g. propane dewaxed. Unless a V.I. improver is incorporated in the blend it is preferable that this oil has a high viscosity index such as an index above 90 and preferably 100.

The following example serves to illustrate the lubricant composition of the present invention.

*Example C*

Product 1, i.e. stabilised phosphosulphurised polymerised olefin: Oronite 32 and 15% by weight of phosphorus pentasulphide were mixed and heated gradually to a temperature of 300° F. Oronite 32 is a homopolymer of isobutylene and has a Staudinger molecular weight of 1,200. The reaction was carried out under a blanket of nitrogen. When the initial reaction had subsided, the temperature was raised to 428° F. and maintained at this higher temperature for 8 hours. 3 wt. percent of gms. of benzoyl peroxide and stirred and heated at 176° F. for 4 hours.

| | Grams |
|---|---|
| Ethoxyl ester | 8 |
| $C_9$ maleic diester | 37 |
| $C_{17}$ Oxo-maleic diester | 37 |
| Vinyl acetate | 18 |

Engine tests have been carried out with a mineral oil without additive and with the same mineral oil containing product 1, product 2 and a mixture of products 1 and 2. The products 1 and 2 were dissolved in a paraffinic SAE 30 mineral oil to give the blends used in the engine test.

These tests were conducted according to the standard CRC FL2 (Co-ordinating Research Council) adapted to a Peugeot 203 engine (4 cylinders, bore 75 mm., stroke 73 mm., total cylinder capacity 1,290 cc.—compression ratio 6.8—speed 2,500 r.p.m.). The time of test was 50 hours. Output 20 H.P. Temperature of oil 131° F., temperature of water inlet 91.4° F., outlet 95° F.

The engine test data, as shown in the table I, of the lubricant blend containing the stabilised phosphosulphurised polymerised olefin and the polymerised alkoxy ester demonstrate the properties of the lubricants of this invention and emphasise that our discovery is based on the unexpected synergism exhibited.

The lubricants of the present invention may also include conventional additives selected from the following: pour point depressants, viscosity index improvers, oiliness carriers, rust preventives, anti-foam agents or dyes.

*Table I*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Oil Formula: | | | | | | | | |
| Paraffin oil, SAE 30, viscosity 118 centistokes at 99° C., viscosity index 137 | 100 | 98 | 98 | 98 | 97 | 97 | 97 | 97.5 |
| Product I | | 2 | | 1 | 3 | | 2 | 2 |
| Product II | | | 2 | 1 | | 3 | 1 | 0.5 |
| Characteristics of the Lubricating Compound: | | | | | | | | |
| Viscosity in centistokes at 99° C | 11.8 | 12 | 12.8 | 12.5 | 12.2 | 13 | 12.7 | 12.5 |
| Viscosity Index | 137 | 138 | 142 | 140 | 138 | 144 | 140 | 139 |
| Pour Point (° C.) | —30 | —30 | —33 | —33 | —30 | —36 | —33 | —30 |
| Results of Engine Tests: | | | | | | | | |
| Cleanliness [1]— | | | | | | | | |
| Combustion Chamber | 7.64 | 8.9 | 8.4 | 8.9 | 8.95 | 8.05 | 8.95 | 9.4 |
| Piston skirts (gummed) | 5.5 | 9.94 | 9.75 | 9.85 | 9.94 | 9.63 | 9.94 | 9.94 |
| Liners (gummed) | 5.75 | 9.5 | 7.5 | 8.4 | 9.65 | 7.38 | 8.48 | 8.73 |
| Tappets gummed | very thick | none | thick | slight | none | thick | slight | very slight |
| Sludge deposit— | | | | | | | | |
| In grammes on oil filter | 29 | 6 | 3.2 | 0.2 | 4.1 | 2.8 | 0 | 0 |
| In grammes on crankshaft | 11 | 7 | 4 | 1.8 | 5.2 | 3.4 | 1.5 | 2 |

[1] The cleanliness of the engine parts listed above, has been rated from 1 to 10, 10 being given to those parts with no deposits and 0 to the parts entirely covered with deposit.

kieselguhr was added and the product was mixed for 1 hour at 266° F. to 284° F. 8 wt. percent of ethylene oxide was absorbed in this reaction mixture at 284° to 302° F. The reaction was completed over a period of 4 hours.

Product 2, i.e. polymerised alkoxy ester: Maleic anhydride, 1 mol, was melted at a temperature of 140° F. to 194° F., and 1 mol of $C_9$ Oxo alcohol was mixed with the molten anhydride. The alcohol was added over a period of 1 hour and the formation of the half ester of maleic acid completed by maintaining the reactants at 140 to 194° F. for 30 minutes.

1% by weight of boron trifluoride as the ether complex was added, as a catalyst, to the half-ester of maleic acid, obtained by the foregoing reaction, and heated to a temperature of 284° F. and 2.5 molecules of ethylene oxide adsorbed therein. The reaction mixture was heated for a further hour at a temperature of 284° F. The composition listed immediately below was mixed with 2

What is claimed is:

1. A lubricating oil composition comprising a major proportion of a mineral lubricating oil, and a synergistic mixture with regard to inhibition of sludge formation of between 0.005 and 6 wt. percent of an alkoxylated phosphosulfurized polybutene and between 0.04 and 9.5 wt. percent of a polymer of an alkoxylated partial ester of an acid selected from the group consisting of fumaric and maleic acid partially esterified with a $C_3$ to $C_{20}$ monohydric alcohol, said phosphosulfurized polybutene being obtained by reacting a sulfide of phosphorus with polybutene having a Staudinger molecular weight of about 900 to 1600 until 2 to 12 wt. percent sulfur and 1 to 7 wt. percent phosphorus is incorporated therein, then reacting said phosphosulfurized polybutene with a $C_2$ to $C_3$ alkylene oxide until an average of 1 to 10 alkylene oxide residues are included in the phosphosulfurized polybutene, and wherein said alkoxylated partial ester is prepared by reacting a $C_2$ to $C_3$ alkylene oxide with said

partial ester until an average of 1 to 10 alkylene oxide residues are incorporated per mole of partial ester.

2. A lubricating oil composition according to claim 1, wherein said alkylene oxide is ethylene oxide, said sulfide of phosphorus is $P_2S_5$, said acid is maleic acid and said alcohol contains 9 carbon atoms.

3. A lubricating oil composition comprising a major proportion of a mineral lubricating oil, about 0.005 to 6 weight percent of a stabilised phosphosulphurised polymerised olefin and about 0.004 to 9.5 weight percent of a polymerised alkoxy ester, the stabilised phosphosulphurised polymerised olefin being obtained by reacting at a temperature within the range of 300 to 550° F. a polymerised olefin having a Staudinger molecular weight in the range of 900 to 1,600 with 5 to 30 wt. percent of a sulphide of phosphorus until a phosphosulphurised derivative is obtained which contains in the range of 2 to 12 wt. percent of sulphur and 1 to 7 wt. percent of phosphorus, subsequently reacting this phosphosulphurised derivative with ethylene oxide at a temperature in the range of 176° F. and 302° F. for a time in the range of 2 to 10 hours until from 1 to 10 ethylene oxide residues are included in the stabilised phosphosulphurised polymerised olefin; the polymerised alkoxy ester having a Staudinger molecular weight in the range of 3,000 to 50,000 and being obtained by reacting a partial ester mixture of maleic acid and an aliphatic monohydric alcohol having 3 to 20 carbon atoms with ethylene oxide at a temperature in the range of 176 to 302° F. for a time in the range of 0.5 to 2 hours to obtain an alkoxy ester having 1 to 10 ethylene oxide residues per mol of alkoxy ester and polymerising this alkoxy ester at a temperature in the range of 140° F. to 212° F. in the presence of a polymerisation catalyst.

4. A lubricating oil composition comprising a major proportion of a mineral lubricating oil, about 0.005 to 6 weight percent of a stabilised phosphosulphurised polymerised olefin and about 0.004 to 9.5 weight percent of a polymerised alkoxy ester, the stabilised phosphosulphurised polymerised olefin being obtained by reacting at a temperature within the range of 300 to 550° F. a polymerised olefin having a Staudinger molecular weight in the range of 900 to 1,600 with 5 to 30 wt. percent of a sulphide of phosphorus until a phosphosulphurised derivative is obtained which contains in the range of 2 to 12 wt. percent of sulphur and 1 to 7 wt. percent of phosphorus, subsequently reacting this phosphosulphurised derivative with ethylene oxide at a temperature in the range of 176° F. and 302° F. for a time in the range of 2 to 10 hours until from 1 to 10 ethylene oxide residues are included in the stabilised phosphosulphurised polymerised olefin; the polymerised alkoxy ester having a Staudinger molecular weight in the range of 3,000 to 50,000 and being obtained by reacting a partial ester mixture of maleic acid and an aliphatic monohydric alcohol having 3 to 20 carbon atoms with ethylene oxide at a temperature in the range of 176 to 302° F. for a time in the range of 0.5 to 2 hours to obtain an alkoxy ester having 1 to 10 ethylene oxide residues per mol of alkoxy ester and copolymerising the alkoxy ester with 15 to 30 wt. percent of a vinyl ester having in the range of 4 to 20 carbon atoms per molecule.

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