This invention relates to the production of oil additives, and particularly to a new process for the production of a detergent additive for a lubricating oil.

Detergent additives are added to what are called "premium" lubricating oils for the purpose of improving their dispersion power, and hence, when they are used in an internal combustion engine, of delaying the onset of piston seizure, the corrosion and wear of the cylinder, and the formation of sludge and carbon deposits.

An improved process for the production of a detergent additive has now been found. Accordingly, the invention comprises a process for the production of a detergent additive for lubricating oil, in which a mixture of a phosphosulfurized polysulfide with an alkylphenol sulfide or an alkylphenol is treated with an oxide or hydroxide of a divalent metal, and the product obtained thereby.

The alkylphenol sulfide (that is to say a compound containing two alkyl phenol residues linked by one or more sulfur atoms) or the alkylphenol is preferably one which has an aromatic nucleus that is substituted by an alkyl group having 5 to 20 carbon atoms, especially from 7 to 12 carbon atoms. An alkyl group having 9 carbon atoms is often satisfactory. The alkyl group can be straight-chain or branched, and is preferably a primary alkyl group.

It is often preferable to use an alkylphenol sulfide rather than the alkylphenol itself. The sulfide is preferably a monosulfide, but disulfides and polysulfides are also useful. A suitable alkylphenol sulfide can in fact be made from an appropriate alkylphenol by reaction with sulfur dichloride, the product usually consisting mainly of alkylphenol monosulfide as well as some oil- or polysulfide.

Examples of suitable alkylphenol sulfide and alkylphenol starting-materials are n-alkyl phenol and dodecylphenol and their mono- or disulfides.

The polyolefin that is used in phosphosulfurized form is a polypropylene or polyisobutylene that has an average molecular weight between 500 and 2500, for example 1100. It can for instance have been phosphosulfurized by reacting it with a phosphorus sulfide such as for example P₂S₅, P₂S₆, or more preferably P₅S₉. The phosphosulfurized polyolefin can be used as such, that is to say in the form in which it is produced by phosphosulfurization.

The alkylphenol sulfide or alkylphenol and the phosphosulfurized polyolefin can be used in any desired relative proportion, but usually it is preferred to employ these in a weight ratio between 1:1 and 1:4, especially between 1:2.5 and 1:3.

The metal oxide or hydroxide is preferably that of an alkaline earth metal, although other divalent metal oxides or hydroxides, for example zinc oxide, can be used if desired. Suitable alkaline earth metal oxides and hydroxides include those of magnesium, calcium and barium. Barium oxide gives excellent results. The oxide or hydroxide is used in an amount sufficient to ensure neutralization of the mixture; however, a slight excess up to 15% by weight can be used.

The process is preferably carried out at a moderately elevated temperature, for example between 40° C. and 80° C., and in the presence of an inert solvent. Liquid hydrocarbons are often suitable solvents, including for example various petroleum fractions such as for instance the naphthenic hydrocarbons and light oils. Oils of various kinds are in fact the preferred solvents. It is preferable to carry out the process in the presence of a lower aliphatic alcohol as an additional solvent, for example methanol, ethanol, isopropanol or butanol; methanol is preferred. Any excess alcohol is preferably removed after the treatment is complete and this can conveniently be done by distillation.

Carbon dioxide can be employed with advantage at some stage in the process as an additional reactant, for this has been found to increase the proportion of divalent metal that can be incorporated into the product.

The presence of water during the process is usually deleterious, and it is desirable that water be excluded as far as possible. For example, the presence of more than 1% by weight of water in the reaction mixture is not well tolerated, and it is therefore preferable to ensure that the components of the reaction system are well dried before use. In particular, if an alcohol is added to the reaction system and partially recovered by distillation, the recovered alcohol can become contaminated with water formed as a by-product in the process, and is therefore usually unsuitable for re-use in the process without first being dried.

The final products of the process of the invention are preferably added to a lubricating oil in an amount corresponding to a divalent metal content of 0.5% to 2% by weight of the final composition, for instance between 0.1% and 1%, especially about 0.5% by weight. Oil compositions containing higher proportions of these products, for instance corresponding to a divalent metal content of up to 15% by weight, especially from 5% to 12% by weight, are also useful as concentrates to be diluted with more oil before use.

The products of the invention can be used alone as lubricating oil additives, but are preferably employed together with a sulfonate detergent additive since this has been found to give a product having superior properties. Suitable sulfonate additives include divalent metal salts of sulfonated aromatic hydrocarbons, for example the barium salt of a sulfonated wax/benzene condensate, or the barium salt of a sulfonic acid obtained by sulfonating the high-boiling residue that is a by-product of the manufacture of dodecylbenzene by the alkylation of benzene with propylene tetramer. The weight of sulfonate additive is preferably not more than 50% of the combined weight of itself and the product of the invention, for example between 10% and 45%, especially between 15% and 30%. About 25% is often a good proportion to use.

The process of the invention is illustrated by the following example.

Example

This example describes the production of a detergent additive according to the process of the invention.

A solution of 132 grams of nonylphenol sulfide in 22 cc. of a mineral oil was mixed with 340 grams of phosphosulfurized polyisobutylene dissolved in 146 cc. of mineral oil. The temperature of the mixture was raised to 65° C., and 100 grams of barium oxide were added over a period of 15 minutes. 120 cc. of methanol were added slowly, and the mixture was refluxed for 3 hours. The methanol was distilled off, and the residue was heated to 150° C. and held under partial vacuum (15 mm. of mercury absolute pressure) for 1 hour. The mixture was then cooled to 65° C., and 50 grams of barium oxide were added over a period of 15 minutes followed by a further 100 cc. of methanol. The mixture was refluxed for 4 hours. The methanol was distilled off and the residue was held under vacuum for 1 hour at 150° C. With the mixture still at 150° C., carbon dioxide gas was fed into it at a pressure of 10 pounds per square inch gauge, after which the mixture was held under...
vacuum (15 mm. mercury pressure) for one hour at 150° C. before allowing it to cool and releasing the vacuum. The product was filtered and diluted with more of the mineral oil until it had a barium content of 10% by weight. It was found to impart excellent detergent properties to mineral lubricating oils to which it was added in an amount corresponding to a barium content of 0.5% by weight.

The detergent properties of the oil were still further improved when there was used a mixed additive comprising 3 parts by volume of the above diluted product and one part by volume of a mineral oil solution of the barium salt of a sulfonated dodecylbenzene/wax/benzene condensation product, the total barium content of the additive being 10% by weight.

For the purpose of comparison, attempts were made to neutralize the phosphosulfurized polyisobutylene in the manner indicated above but in the absence of the nonylphenol sulfide. There was obtained a product of a stiff consistency that was exceedingly difficult to filter. What is claimed is:

1. A process comprising reacting at temperatures in the range of about 100° F. to about 300° F. a mixture of 
(a) a phosphosulfurized olefin polymer, said polymer having a molecular weight of from about 500 to 2500 and 
(b) a compound selected from the group consisting of an alkylphenol and an alkylphenol sulfide in each of which the alkyl group has from 5 to 20 carbon atoms, with 
(c) at least about an amount sufficient to neutralize said mixture of an oxide or hydroxide of a metal selected from the group consisting of zinc, magnesium, calcium and barium in the presence of a lower alkanol having from 1 to 4 carbon atoms, the weight ratio of (a) to (b) being about 1:1 to about 4:1, respectively.

2. Claim 1 where (a) is a phosphosulfurized polyisobutylene.

3. Claim 1 where (b) is nonylphenol sulfide.

4. Claim 1 where (c) is barium oxide and the alkanol is methanol.

5. A process comprising reacting at temperatures in the range of about 100° F. to about 300° F. a mixture of 
(a) a phosphosulfurized polyisobutylene, said polyisobutylene having a molecular weight of about 1100 and 
(b) nonylphenol sulfide with 
(c) at least about an amount sufficient to neutralize said mixture of barium oxide in the presence of methanol, the weight ratio of (a) to (b) being about 1:1 to about 4:1, respectively.

6. The product prepared by the process of claim 1.

7. The product prepared by the process of claim 8.

8. A composition comprising a major amount of a lubricating oil and a minor amount of the product of the process of claim 1.

9. A composition comprising a major amount of a lubricating oil and a minor amount of the product of the process of claim 5.

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