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METAL AND SULFUR CONTAINING COMPOUNDS AND LUBRICANTS CONTAINING THEM

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This invention relates to metal and sulfur-containing phenolic-type compounds having improved stability and reduced corrosiveness. More particularly, it relates to an improved process for producing such materials and to the use of the materials as additives for lubricants, fuels and the like.

It is well known in the art to employ metal and sulfur-containing derivatives of phenolic-type compounds as additives for mineral oils and the like. Such additives include the sulfurized and phosphosulfurized derivatives of metal phenates and thiophenates, and the metal salts of hydroxy and mercapto substituted aromatic sulfides and their sulfurized and phosphosulfurized derivatives. These compounds improve various properties of lubricants such as improving detergent action in engines to promote engine cleanliness, increasing oil film strength, reducing ring sticking, inhibiting deterioration of the oil by oxidation and the like.

During recent years, the trend has been toward using increased concentrations of detergent-type additives in lubricants. This trend has been necessitated by the need for high grade lubricants meeting rigid specifications required for service in modern engines that operate at relatively high temperatures and speeds. The metal salts of sulfur-containing phenolic-type compounds are frequently unsuitable for use in relatively high concentrations. In some cases they corrode alloy bearings, such as those of cadmium-silver and copper-lead, so widely used in automotive and Diesel engines as well as other copper, brass or bronze parts used in the engines. In other cases, such compounds are substantially non-corrosive in themselves, but a combination of them with other additives, such as oil-soluble metal petroleum sulfonate, may be excessively corrosive. In addition, these compounds sometimes evolve hydrogen sulfide in sufficient quantities to impair the odor of the additives or of lubricants containing them.

It is a principal object of the present invention to provide a means for reducing the corrosiveness and increasing the stability of the derivatives of phenolic-type compounds. The practice of this invention permits the use of high concentrations of the additives in lubricants, improves the compatibility of such additives with other types of additives, and reduces the odor of these compounds.

In accordance with the present invention, a metal and sulfur-containing derivative of a phenolic-type compound is heat-treated during at least one stage of its preparation with a stabilizing agent selected from the class of organic rubber vulcanization accelerators. The treatment is carried out at an elevated temperature of at least 275° F. and below about 600° F., preferably in the range of about 300° F. to 500° F. The heating step is continued for a period of time sufficient to improve the stability and reduce the corrosiveness of the material. A time in the range of about 0.5 to 20 hours, preferably 3 to 15 hours, will generally be adequate.

The improvements obtained in the practice of the present invention are not understood. It is known that various alkyl phenol sulfides are powerful vulcanizing agents for making rubber, releasing active sulfur during vulcanization, and they are frequently used as a total replacement for sulfur. The various known rubber vulcanization accelerators aid in this process. Stabilization of the compounds of the present invention obviously follows an entirely different reaction mechanism since metal alkyl phenol sulfides and their sulfurized derivatives, for example, are stabilized by the vulcanization accelerator without any substantial loss in total sulfur content. The fact that accelerators aid decomposition of such compounds in rubber manufacture and stabilize related compounds in the present invention is quite unexpected.

The compounds of the present invention may be prepared by several procedures. For example, a metal salt of a phenolic-type compound may first be formed and then treated with a sulfurizing agent, such as sulfur, a sulfide of phosphorus and the like, to obtain a sulfur-containing derivative. The stabilizing agent may be present during the actual sulfurization step or may be added after the sulfurization reaction is substantially complete. In this latter instance, the sulfur-containing derivative is after-treated with the stabilization agent at appropriate conditions. If desired the stabilization agent may be present during the sulfurization step, and additional agent may be used in an after-treating step.

In another aspect of this invention, a sulfide of a phenolic-type compound may first be formed by treatment with a sulfurizing agent such as a sulfur chloride. A metal salt derivative is then formed. A stabilization agent may be used during the formation of the sulfide, although it is generally preferred to after-treat the metal salt of the phenolic-type sulfide with the stabilization agent. Particularly desirable compounds are produced by treating the metal phenol sulfides with a sulfurizing agent such as sulfur, a sulfide of phosphorus, etc. The use of a stabilizing agent during and/or after the sulfurizing step is quite beneficial.

The step or steps at which the stabilizing agent is used during the preparation of the compounds will depend on a number of factors. These include the type of sulfur-containing derivative being produced, the degree of stabilization required, the type of sulfurization agent being used, etc. However, the instability and corrosiveness of such compounds arises as a result of introducing sulfur therein. Therefore, the stabilizing agent should be present during at least one step of the preparation of the sulfurized derivative, i. e., during a sulfurization step, during an after-treating step on the sulfurized product or during or after a resulfurization step on the sulfurized product.

The class of compounds suitable as stabilizing agents in the present invention are well known to the art as rubber vulcanization accelerators. Such materials are discussed in "Compounding Ingredients For Rubber," Second Edition, 1947, compiled by the editors of India Rubber World. Specific classes of compounds include thiazole derivatives such as the mercaptobenzothiazoles; aryl guanidine derivatives such as di-orthotolylguanidine, diphenyl and triphenyl-guanidines and mixtures of aryl guanidines; dithiocarbamate derivatives such as piperidinium pentamethylene dithiocarbamate, 2,4-dinitrodimethyl dithiocarbamate, and the zinc, copper, selenium and tellurium salts of dialkyl dithiocarbamates such as of diethyldithiocarbamate; sulfide derivatives of the above and other compounds, such as benzothiazyl disulfide, tetraethylthiuram disulfide, tetramethylthiuram mono- and tetrasulfides, and dibutyl xanthogen disulfide; amino-aldehyde condensation products such as those of aniline

and formaldehyde, toluidine and various aldehydes, and of aniline and acetaldehyde; thiourea derivatives such as symmetrical diphenylthiourea; nitroso derivatives such as a polymer of p-nitrosobenzene; xanthates such as zinc butyl-xanthate, and the like.

The derivatives of dithiocarbamic acids are generally preferred in the practice of the present invention, although the aryl guanidines are also quite useful.

The stabilizing agents may be used singly or in combination. For example, mixtures of mercaptobenzothiazole and diphenyl guanidine are quite effective. The quantity of stabilizing agent needed will vary depending on the particular agent being used and the material being treated. Amounts in the range of about 0.1 to 20% by weight, preferably about 1% to 10% by weight, based on the phenolic derivative being treated, will generally suffice.

The phenolic-type compounds used to prepare the derivatives of the present invention have the general basic formula: R Ar XH, wherein R represents at least one hydrocarbon substituent group, preferably an alkyl radical, such as butyl, amyl, hexyl, tert.-octyl, decyl, dodecyl and the like, attached to the aromatic nucleus Ar. The R radical preferably has at least 4 carbon atoms, especially if oil solubilizing properties are desired. Preferably R radicals will have 5 to 20 carbon atoms in a single or plurality of groups. Ar may be a benzene nucleus, a plurality of rings such as naphthalene and anthracene, and the like. X in the formula is selected from the group consisting of oxygen and sulfur and is preferably oxygen. The term "phenolic-type compound" as used herein refers however to phenols and thiophenols.

The metal derivatives of the phenolic-type compounds may then be formed if desired before sulfurization. Such derivatives, known as metal phenates and metal thiophenates, are preferably of the divalent metals of Group II of the periodic table. These include calcium, barium, strontium, magnesium, and zinc. Derivatives of tin, lead, cobalt, nickel, etc. will also be useful for some purposes. These metal derivatives are formed by procedures well known in the art.

In other cases, it will be preferable to form first the metal salt of a phenol or thiophenol sulfide. The sulfide is conveniently formed by the conventional procedure, i. e. treating the phenolic compound with a sulfur halide such as sulfur chloride or sulfur dichloride. The metal salt may then be formed by treating the phenol sulfide with a basic reacting divalent metal reagent or the like. This metal salt may be treated with the stabilizing agent of the present invention as heretofore described. The treated salt has improved anti-corrosion characteristics, and the combination of it with oil-soluble metal petroleum sulfonate is much less corrosive than a similar combination including the untreated salt.

The invention has particular application also to the derivatives formed by treating the metal phenates and metal phenol sulfides with a sulfurizing agent, such as elemental sulfur, combinations of elemental sulfur and phosphorus, sulfides of phosphorus such as P_2S_5, P_4S_3, P_4S_7, and to various combinations of these. When sulfurizing with elemental sulfur, about 1 to 4 atomic proportions of sulfur for each atomic proportion of metal may be used. When phosphosulfurizing, about 0.05 to 2 atoms of phosphorus are reacted with one atom of metal, using about 0.75 to 2.5 atomic proportions of sulfur for each atomic proportion of metal. Temperatures for the various sulfurization reactions may vary in the range of about 200° F. to 450° F. for a time sufficient to complete the reaction. As mentioned previously, the stabilization agent may be present during the sulfurization step. If sulfurization is carried out in the lower part of the above-mentioned range in the presence of a stabilizing agent, the reaction products should then be heated at a temperature above about 375° F. in order to obtain the amount of stabilization desired. Additional stabilization agent may be added during this heating step. It is generally preferred, however, to add the stabilization agent to the sulfurized product and heat treat at a higher temperature than that used during sulfurization.

The preparation of the metal and sulfur-containing derivatives of such phenolic compounds is taught in the art, and specific details need not be given herein. Sulfurization and phosphosulfurization of metal alkyl phenates and the like are taught in U. S. 2,406,564 and U. S. 2,409,686, issued, respectively, in the name of Dilworth T. Rogers on August 27, 1946, and John G. McNab and Dilworth T. Rogers on October 22, 1946. The sulfurization and phosphosulfurization of metal alkyl phenol sulfides and the like are taught in U. S. 2,409,687, 2,451,346, 2,483,505, and 2,518,379, all issued in the names of Dilworth T. Rogers and John G. McNab.

Generally, the additives of the present invention are most advantageously blended with mineral oils such as lubricating oil base stocks in concentrations between the approximate limits of 0.02% and 20% and preferably from 0.1% to 10.0%, although larger amounts may be used for some purposes. The exact amount of addition agent required for maximum improvement depends to a certain extent on the particular products used, the nature of the lubricating oil base stock and the general operating conditions of the engine in which the lubricant is to be employed. This same general range of concentration will also be effective when the additives are to be used in greases and in extreme pressure lubricants, although in the latter instance amounts above about 10% may be needed.

It is often convenient to prepare concentrates of the additives in oil, containing a minor amount, such as 25% to 50% of effective addition agent, the concentrate later being added to a suitable lubricating oil base stock to give a finished blend containing the desired percentage of additive. Thus, when using a 40% concentrate, 2.5% of this material will be blended with a suitable base stock to give a finished oil containing 1% of effective addition agent.

The lubricating oil base stock used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloroethyl ether, propane, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coal tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed, either alone or in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additives present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which

they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of diesel service, particularly with high speed diesel engines, and in gasoline engines, including aviation engine service, oils of higher viscosity index are often preferred, for example, up to 75 and 100, or even higher, viscosity index.

The products of the present invention are particularly effective when used in conjunction with oil soluble petroleum sulfonates as lubricant additives. Such combined additives are extremely effective detergent agents. Furthermore, whereas such prior art combinations are frequently corrosive to metals, the treated products of the present invention form substantially non-corrosive mixtures with the sulfonates. Suitable metal sulfonates are those produced by conventional procedures, such as by acid treatment of mineral oils, followed by extraction and neutralization of the recovered sulfonates. Salts of metals such as calcium, sodium, barium, strontium, aluminum and the like are suitable. Alkaline earth metal salts are preferred. The lubricant may include in the range of about 0.1% to 10.0% by weight of the metal petroleum sulfonates.

In addition to the above materials to be added according to the present invention, other agents may also be used, such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, anti-oxidants, thickeners, viscosity index improvers, oiliness agents, resins, natural or synthetic rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like, may also be employed.

In addition to being employed in crankcase lubricants the additives of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, process oils, general machinery oils, greases and rust preventive compositions. Also their use in motor fuels, diesel fuels and kerosene is contemplated. A particular application in this regard is their use in motor fuels containing tetraethyl lead or other anti-knock agents.

Various preparations of products and the results obtained by testing them are described in the following examples. It is to be understood that these examples are given for illustrative purposes only and do not limit the scope of the invention in any way.

Example I.—Treatment of metal alkyl phenol sulfide with stabilizing agent

Barium tert.-octyl phenol sulfide was prepared in the conventional manner by treating tert.-octyl phenol with sulfur dichloride followed by neutralization of an oil solution of the resulting tert.-octyl phenol sulfide with barium hydroxide pentahydrate. The oil concentrate contained about 40% by weight of barium tert.-octyl phenol sulfide and analyzed about 9% by weight barium and about 3.4% by weight sulfur.

A portion of the resulting oil concentrate was then treated with a stabilizing agent by blending therewith 2.5% by weight of mercaptobenzothiazole ("Captax") and 1.25% by weight of diphenylguanidine ("DPG") and heating the blend at a temperature of 350° F. for 3 hours. The percent concentrations of "Captax" and "DPG" were based on the metal phenol sulfide.

Oil blends were prepared containing 12% by weight of both the treated and untreated oil concentrates in a diesel-type lubricant having a viscosity of about 900 S. S. U. at 100° F. Another series of blends were prepared as above and including in addition 1.8% by weight of conventionally produced oil-soluble calcium petroleum sulfonate.

The above blends were subjected to the silver corrosion test by observing the discoloration and weight change of a sterling silver strip after immersion in 50 cc. of the oil blend for 17 hours at 325° F. Strain is rated from "1" (no discoloration) to "8" for a complete sulfide film. A Fail rating is given where stain and/or weight changes are excessive. The results of these tests are presented in Table I, below:

TABLE I

Oil Blend	Components of Oil Blend			Silver Corrosion Rating
	Barium tert.-octyl phenol sulfide—oil concentrate		Calcium Petroleum Sulfonate—oil Concentrate,[1] Wt. Percent	
	Treated with stabilizing agent	Wt. Percent in Blend		
1	No	12	0	3 (Pass).
2	Yes	12	0	2 (Pass).
3	No	12	6	7 (Fail).
4	Yes	12	6	3 (Pass).

[1] 30% sulfonate in oil.

Treatment of the metal alkyl phenol sulfide with a rubber vulcanization accelerator effected a slight improvement in its silver corrosion characteristics as shown by ratings on oil blends containing only this component. A striking improvement was obtained however when the treated additive was used in conjunction with calcium petroleum sulfonate. It is apparent that treatment of metal phenol sulfides with a stabilizing agent of the rubber vulcanization accelerator type improves the compatability of these materials and of other types of more or less corrosive lubricant additives insofar as corrosion characteristics are concerned.

Example II.—Stabilization of phosphosulfurized metal alkyl phenol sulfide

Product A.—A portion of the untreated oil concentrate of barium tert.-octyl phenol sulfide (Example I) was treated with 4% by weight of phosphorus pentasulfide (P_2S_5) at a temperature of about 300° F. for one hour in an inert atmosphere of nitrogen. The reaction product was then heat soaked for 5 hours at 300° F., blown with nitrogen for 2 hours at the same temperature, and filtered while hot through "Hi-flo," a diatomaceous filter aid.

Product B.—This product was prepared by the procedure used in preparing Product A except that 12.5% by weight of mercapto benzothiazole ("Captax"), based on the metal phenol sulfide was added during a 5-minute period at 300° F. before treatment with P_2S_5.

Product C.—This product was prepared by the procedure used in making Product A except that 12.5% by weight of mercapto benzothiazole, based on the metal phenol sulfide, was added to the heat soaked and nitrogen blown material (before filtering), heat soaked for an additional 90 minutes at 300° F. and then filtered.

The above products were analyzed. They were also tested for H_2S evolution characteristics by measuring the extent of staining of a paper dipped in saturated lead acetate solution. The results are shown in Table II below.

TABLE II

Product	A	B	C
Treated with "Captax"	No	Yes	Yes
Analysis, Wt. Percent:			
Barium	8.49	7.98	7.68
Sulfur	6.27	7.36	6.96
Phosphorus	1.06	0.98	1.03
H_2S Rating	Fail	Pass	Pass

The stability of the phosphosulfurized metal phenol sulfide was greatly improved by employing a stabilizing agent either during or subsequent to the phosphosulfurization step. For a given amount of phosphosulfurization agent, it is noted that Product B contains about 20% more sulfur and Product C about 10% more sulfur than Product A. This gaves a more favorable ratio of sulfur to phosphorous in the product.

Example III.—Stabilization of phosphosulfurized metal alkyl phenol sulfide.

Product D.—This product was prepared substantially in accordance with the procedure used in making Product A (Example II). This product contained a 40% concentration of phosphosulfurized barium tert.-octyl phenol sulfide in oil.

Product E.—A portion of Product D was treated with a mixture of 2.5% by weight of "Captax" and 1.25% by weight of "DPG" at about 350° F. for 2½ hours and then for 6 hours at 400° F.

Each of the above products were blended in an S. A. E. 20 base lubricant to the extent of 2% by weight of each oil concentrate. The blends were then tested for silver corrosion characteristics by the procedure described in Example I. The blend containing Product D gave a complete black sulfide film and received a rating of 8 (fail). The Product E blend passed the test with a rating of 3. Obviously, heat-treatment of the phosphosulfurized metal phenol sulfide with a stabilizing agent of the character described effected a substantial decrease in its corrosiveness.

This improvement was confirmed in a laboratory bearing corrosion test conducted in accordance with the procedure described in Example 12 of U. S. 2,529,303 issued in the name of John P. McDermott on November 7, 1950. Blends were prepared containing 0.25% by weight of the active ingredient of Products D and E in an S. A. E. 20 grade base oil and tested for their corrosiveness towards copper-lead bearings. The results are given in Table III, below as "Bearing Corrosion Life" showing the number of hours required for each bearing to lose 100 milligrams in weight.

TABLE III

Product used in Oil Blend	Bearing Corrosion Life, Hours
None	9
D	26
E	32

Example IV.—Stabilization of sulfurized metal alkyl phenate

Product F.—This product was prepared in the conventional manner by treating an oil solution of a metal phenate, barium tert.-octyl phenol, with elemental sulfur at a temperature of about 270° F. The product comprised a 40% solution of the sulfurized barium phenate in oil and analyzed about 9% by weight barium and 3.5% by weight sulfur.

A portion of Product F was heat-treated for 3 hours at 350° F.

Other portions of Product F were heat-treated in the presence of 2.5% by weight of "Captax" and 1.25% by weight of "DPG" for 1, 2, and 3 hours, respectively at 350° F. (concentrations based on sulfurized metal phenate). Oil blends containing 3.5% by weight of each of the heat-treated products (40% solutions) in an S. A. E. 30 base oil were prepared and tested for silver corrosion characteristics by the procedure outlined in Example I. The results are shown in Table IV.

TABLE IV

Treating Conditions at 350° F.		Silver Corrosion Rating
Stabilizing Agent Present	Treating Time, Hours	
No	3	7 (Fail).
Yes	1	7 (Fail).
Yes	2	4 (Pass).
Yes	3	2 (Pass).

The sulfurized metal alkyl phenate, even after heat-treating for 3 hours, was extremely corrosive. Heat-treatment in the presence of a stabilizing agent produced a satisfactory product after 2 hours and a substantially non-corrosive product after 3 hours.

What is claimed is:

1. In a process of producing a derivative, containing both alkaline earth metal and sulfur atoms, of an alkyl phenol containing 5 to 20 carbon atoms in the alkyl group wherein the sulfur is introduced into said derivative by at least one sulfurizing agent selected from the group consisting of sulfur chlorides, elemental sulfur and sulfides of phosphorous, the improvement which comprises treating said derivative with a stabilization agent selected from the group consisting of mercaptobenzothiazole, diphenylguanidine and mixtures thereof in an amount in the range of about 0.1% to 20% by weight based on said derivative, said treatment being carried out at a temperataure in the range of about 275° to 600° F. for a time sufficient to produce a substantially stable, non-corrosive product.

2. In a process of producing a derivative, containing both barium and sulfur atoms, of an alkyl phenol having 5 to 20 carbon atoms in the alkyl group wherein the sulfur is introduced into said derivative by at least one sulfurizing agent selected from the group consisting of sulfur chlorides, elemental sulfur and sulfides of phosphorus, the improvement which comprises treating said derivative with a stabilization agent selected from the group consisting of mercaptobenzothiazole, diphenylguanidine and mixtures thereof in an amount in the range of about 1 to 10% by weight based on said derivative, said treatment being carried out at a temperature in the range of about 300 to 500° F. for a period of time in the range of about 3 to 15 hours.

3. A process as in claim 2 wherein said alkyl phenol is tert. octyl phenol.

4. A an improved composition of matter, a derivative, containing both alkaline earth metal and sulfur atoms, of an alkyl phenol having 5 to 20 carbon atoms in the alkyl group wherein the sulfur has been introduced into said derivative by at least one sulfurizing agent selected from the group consisting of sulfur chlorides, elemental sulfur and sulfides of phosphorus, said derivative having been treated with a stabilization agent selected from the group consisting of mercaptobenzothiazole, diphenylguanidine and mixtures thereof in an amount in the range of about 0.1% to 20% by weight based on said derivative, said treatment being carried out at a temperature in the range of 275° to 600° F. for a time sufficient to produce a substantially stable, non-corrosive product.

5. As an improved composition of matter, a derivative, containing both barium and sulfur atoms, of an alkyl phenol containing 5 to 20 carbon atoms in the alkyl group wherein the sulfur is introduced into said derivative by at least one sulfurizing agent selected from the group consisting of sulfur chlorides, elemental sulfur and sulfides of phosphorus, said derivative having been treated with a stabilization agent selected from the group consisting of mercaptobenzothiazole, diphenylguanidine and mixtures thereof in an amount in the range of about 1% to 10% by weight based on said derivative, said treatment being carried out at a temperature in the range of about 300° to 500° F. for a period of time in the range of about 3 to 15 hours.

6. A composition of matter as in claim 5 wherein said alkyl phenol is tert. octyl phenol.

7. A composition of matter as in claim 5 wherein said derivative is barium tert. octyl phenol sulfide.

8. A composition of matter as in claim 5 wherein said derivative is the reaction product of barium tert. octyl phenol sulfide and phosphorus pentasulfide.

9. A composition of matter as in claim 5 wherein said derivative is the reaction product of barium tert. octyl phenol and elemental sulfur.

10. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and about 0.02 to 20% by weight, based on the total composition, of a composition of matter defined by claim 4.

11. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and in the range of about 0.1 to 10% by weight, based on the total composition, of a composition of matter defined by claim 5.

12. A lubricating oil composition as in claim 11 which includes a minor, detergency-improving amount of an oil-soluble alkaline earth metal petroleum sulfonate.

13. A additive concentrate consisting essentially of a mineral lubricating oil and about 25 to 50% by weight of a composition of matter defined by claim 4.

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