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COMPOUNDED LUBRICATING OIL

John G. McNab, Cranford, and Dilworth T. Rogers, Summit, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

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This invention relates to addition agents suitable for modifying the properties of organic materials such as petroleum products, and it relates more particularly to lubricating oil compositions for use as crankcase lubricants for internal combustion engines and to addition agents suitable for retarding the deterioration of such oils and for improving other properties of the same.

It is known that the addition of certain types of metal organic compounds to lubricating oils improves various properties thereof, such as their oiliness characteristics and their detergent action in engines, particularly manifested in the maintenance of a clean engine condition during operation. Various metal compounds which have been used for such purposes include the metal derivatives of such organic compounds as fatty acids, naphthenic acids, sulfonic acids, alcohols, phenols, and ketones. However, these various metal compounds generally have the disadvantage of tending to corrode alloy bearings, such as those of cadmium-silver and copper-lead, now so widely used in automotive engines; and this is especially true in engines which operate at relatively high speeds and high temperatures. It is an object of the present invention to provide a new class of addition agents for oils which are to be used as crankcase lubricants for internal combustion engines and which exhibit the desirable properties of promoting general engine cleanliness, improving film strength, reducing ring sticking, piston skirt varnish formation and the like, and which do not exhibit the corrosion promoting tendencies characteristic of the above metal compounds.

The new class of products which have now been found to be highly satisfactory as addition agents are the products obtained by the reaction of elemental sulfur with metal salts of sulfonic acids. Any type of sulfonic acid salt may be used, provided the compound has oil solubilizing groups, such as aliphatic carbon chains. A particularly useful form of sulfonic acid salt is a salt of petroleum sulfonic acids, particularly a salt containing an alkaline earth metal. Thus, a new class of additives is provided which can be formed from cheap and readily available raw materials. The products of the reaction of the metal sulfonates with sulfur are adaptable to use with a wide variety of petroleum lubricating oil base stocks. The reaction for the preparation of the additives may generally be brought about in a solution of lubricating oil or other petroleum oil, whereby concentrates may be prepared which

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may be conveniently stored or shipped and added to lubricating oils when required.

The exact structure of the compounds obtained by the reaction of sulfur with metal sulfonates is not fully understood, but it is possible that compounds are formed in which the sulfur atoms are attached directly to the metal atom.

The metal which is present in the salt which is reacted with elemental sulfur in accordance with the present invention may be any metal, but a highly preferred group of salts are those containing metals of group II of the periodic table, the alkaline earth metal salts being especially useful.

The sulfonic acids from which the metal salts may be derived may be of any type, whether aromatic or aliphatic. The latter include the sulfonic acid derivatives of unsaturated aliphatic hydrocarbons which contain either short or long, straight or branched carbon chains. Although sulfonic acid mixtures derived from petroleum in the treatment of petroleum products with sulfuric acid are exceptionally useful for the purposes of the present invention, other types which may be used include cycloalkyl sulfonic acids, such as the naphthene sulfonic acids, as well as benzene sulfonic acid, naphthalene sulfonic acid, terpene sulfonic acids, and the like. Also to be included are the various derivatives of benzene sulfonic acid and other aromatic sulfonic acids obtained by substituting various groups in the aromatic nucleus, such as alkyl, cycloalkyl, aralkyl, aryl, carboxyl, hydroxyl, mercapto, alkoxy, aroxy, nitro, ester, keto, amino, aldehydo, chloromethyl, aminomethyl, and similar groups, as well as halogen atoms, etc. Different types of atoms or groups may be attached to the same aromatic nucleus, and metal atoms may be substituted for hydrogen atoms in the hydroxyl, carboxyl, or like groups. Particularly suitable are the metal salts of alkylated phenol sulfonic acids. Also included are the metal salts of sulfonic acid derivatives of phenol sulfides, thiophenol sulfides and metal salts thereof, as well as alkylated and other substituted derivatives thereof.

As has already been stated, sulfonic acids whose metal salts are particularly useful for the purposes of the present invention are those derived from petroleum, particularly the so-called mahogany acids which are normally produced during the acid treatment of lubricating oil fractions. Large quantities of these sulfonic acids occur as by-products in the manufacture of white oils by treatment of lubricating oil distillates with concentrated or fuming sulfuric acid. These

sulfonic acids are believed to be mixtures of alkylated aromatic sulfonic acids and may also contain hydroaromatic sulfonic acids and, in some instances, minor proportions of naphthene sulfonic acids and/or olefin sulfonic acids. The lower molecular weight acids can be extracted from the acid treated oil by adding a small amount of water, preferably after dilution of the oil with a petroleum distillate such as kerosene. However, the more desirable high molecular weight (350 to 500) acids, particularly those produced when treating for white oil with fuming acid, are usually recovered commercially as sodium soaps by neutralizing the acid oil with sodium carbonate and extracting the neutralized oil with aqueous alcohol. The crude soap extract is first recovered as a water curd after removal of alcohol by distillation and a gravity separation of some of the contaminating salts (e. g., sodium carbonate, sulfate and sulfite). The material still contains considerable quantities of salts and consequently is normally purified by readdition of alcohol followed by storage to permit settling of a salt brine. The alcohol and water are then stripped out and replaced with a light lubricating oil to yield the commercial purified concentrate, generally containing from 30 to 70% sodium sulfonate.

The following are typical representatives of sulfonic acids whose metal salts may be reacted with sulfur to produce useful additives for lubricating oils in accordance with the present invention:

Calcium mahogany sulfonates
Barium mahogany sulfonates
Strontium mahogany sulfonates
Zinc mahogany sulfonates
Calcium salt of wax-alkylated naphthyl amine sulfonic acid
Tin salt of stearyl benzene sulfonic acid
Calcium cetyl phenol sulfonate
Barium salt of di-tert.-amyl phenol sulfonic acid
Calcium double salt of octadecyl phenol sulfonic acid
Aluminum tert.-octyl phenol sulfide sulfonate
Barium tetraisobutenyl sulfonate
Magnesium oleyl sulfonate
Calcium salts of wax olefin sulfonic acids
Mixed calcium-zinc double salt of isododecyl hydroxyphenyl propane sulfonic acid

For converting sulfonic acids to metal salts, it is often sufficient merely to add a metal or metallic oxide, hydroxide, sulfide, alkoxide, hydride or carbide to a solution of the sulfonic acid at an elevated temperature. Thus, for example, an alkyl phenol sulfonic acid can be converted into its calcium salt by dissolving it in petroleum naphtha and treating it with calcium hydroxide; or mahogany sulfonic acids can be dissolved in ether and treated with barium hydroxide to prepare the barium salts. Likewise, acid treated mineral oils may be neutralized directly with an oxide or hydroxide of a polyvalent metal.

The method usually most convenient for preparing polyvalent metal sulfonates is that of conversion of sodium sulfonates by double decomposition. For example, calcium sulfonates may be prepared by reaction of an aqueous solution of calcium chloride with an aqueous-alcoholic solution of sodium mahogany sulfonates. The precipitated calcium sulfonates are then washed with water to remove inorganic salts. Dehydration of the sulfonates can be conducted conveniently by adding mineral oil to the calcium sulfonate-water mixture and heating to about 240–300° F., the dehydrated product thus being obtained as an oil concentrate containing, say, about 20–30% of calcium sulfonates. If foaming is encountered during dehydration, it can be reduced to a negligible amount by adding a small quantity of a suitable defoaming agent. The oil solutions of polyvalent metal sulfonates obtained in the above-described manner may be treated directly with sulfur by the methods of the present invention.

In addition to the normal polyvalent metal salts of sulfonic acids, it is also contemplated to employ in the present invention the so-called complexes or coordination compounds which metal sulfonates form with other metal salts, particularly inorganic salts, under certain reaction conditions. If when converting a sodium mahogany sulfonate to a polyvalent metal derivative by the methods outlined above, some of the inorganic salt employed for the conversion is allowed to remain during the final dehydration step, a portion of the excess salt forms a complex, or coordination compound, with the sulfonate. This complex, being oil-soluble, remains in solution during filtration of the final oil blend. Other coordination compounds may be prepared by adding to the polyvalent metal sulfonate other metal salts or oxides or hydroxides in addition to or in place of the inorganic salt remaining from the conversion of the sodium sulfonate to a polyvalent metal salt. For example, if sodium sulfonate has been converted to calcium sulfonate, excess calcium chloride may be allowed to remain, and then before dehydration calcium hydroxide may also be added. Or, if a different type of coordination compound is to be formed, the excess calcium chloride from the conversion step may be removed by water washing or by other suitable means, and other materials such as aluminum acetate or lithium chloride may be added before the dehydration step. Sulfonates prepared by direct neutralization of sulfonic acids may be similarly converted to coordination compounds by emulsifying concentrated or dilute oil solutions of the sulfonates with aqueous solutions or suspensions of any suitable salt or base followed by dehydration in the manner already described.

Among the metal sulfonate complexes which may be employed in the present invention are included the following:

Calcium mahogany sulfonate-calcium chloride-calcium hydroxide
Barium mahogany sulfonate-lithium hydroxide-lithium nitrate
Calcium mahogany sulfonate-ammonium chloride
Magnesium mahogany sulfonate-barium hydroxide-calcium chloride

In accordance with the present invention, the metallic salt of a sulfonic acid is caused to react with sulfur. This may be accomplished by adding the sulfur in elemental form to a heated solution of the sulfonate. Sulfur may be used in any of its allotropic forms. In carrying out this reaction the proportions of sulfur and metal salt are so chosen that from 0.02 to 3 atomic proportions of sulfur are reacted with one atomic proportion of metal, the preferred ratio being within the limits of about 0.1 to 2.5 atomic proportions of sulfur for each atomic proportion of metal. Reaction temperatures are preferably within the range of about 90 to 210° C. It is generally convenient to carry out the reaction with the aid of solvents, particularly high boiling hydrocarbon solvents, such as xylol or a petroleum fraction. A particu-

larly preferred reaction medium is a lubricating oil fraction, since the final reaction product can thus be obtained as a mineral oil concentrate of the desired additive, which may be conveniently shipped or stored as such and then readily blended with the lubricating oil base stock in the desired concentration to form a finished lubricating oil blend.

The additives may generally be prepared by first dissolving a sulfonic acid, such as petroleum sulfonic acid, in a mineral oil or other suitable solvent and treating the same with a metal oxide or hydroxide, e. g., CaO or $Ba(OH)_2.2H_2O$, at about 20–150° C., preferably 80–120° C. After a further period of heating free sulfur is added, heating being continued at 80–200° C., preferably at 140–180° C., to complete the reaction. The period of heating may generally be from about ½ hour to about 5 hours, although in some cases a longer period may be required. When the material will no longer stain a strip of copper immersed in it for 10 seconds at 180–190° C., the reaction is considered complete. The product is then filtered, giving a concentrate of the desired additive. If the products are found to have a slight odor of hydrogen sulfide, this can be substantially eliminated by blowing with air or inert gas or by treating with a small proportion (2–5%) of barium hydroxide or calcium oxide or hydroxide at 150° C., followed by filtering and blowing with nitrogen at 100–120° C.

It is sometimes desirable to prepare these additives in the presence of a minor proportion of a higher alcohol, such as stearyl, lauryl or cetyl alcohol, or wool fat alcohol, or the like.

Products with modified properties can often be obtained when carrying out the reaction with sulfur in the presence of a small proportion of an olefinic material, such as tetraisobutylene, cracked wax, styrene, butadiene, terpenes, unsaturated alcohols, such as oleyl alcohol, etc.

It has been found that it is often advantageous to react the sulfonate salt with both free sulfur and a sulfide of phosphorus, such as P_2S_5, P_4S_3, P_4S_7, or the like. The phosphorus sulfide may be reacted with the sulfonate before, simultaneously with, or after the reaction with free sulfur. If a phosphorus sulfide is employed, it is preferable to use from 0.1 to 1 atomic proportions of phosphorus for each atomic proportion of free sulfur.

Generally, the additives of the present invention are most advantageously blended with lubricating oil base stocks in concentrations between the approximate limits of 0.02% and 5.0% and preferably from 0.1% to 2.0%, 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 greater amounts, up to 20%, may also be employed.

However, as has been pointed out elsewhere in this specification, it is often convenient to prepare concentrates of the additives in oil containing, say, 25–75% of the 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 may be blended with a suitable base stock to give a finished oil containing 1% of effective addition agent.

In the following examples are described the various preparations of products in accordance with this invention and the results obtained on testing the same in lubricating oil blends. It is to be understood that these examples, given for illustrative purposes only, do not limit the scope of the invention in any way.

Example 1

Barium mahogany sulfonate

The starting material for this preparation was a 50% aqueous isopropyl alcohol extract containing about 28% of sodium mahogany sulfonates obtained as a by-product in the manufacture of white oils by treating extracted naphthenic oils with 100% sulfuric acid. One gallon of the alcohol extract was heated on the steam bath to remove the solvent, and the residue was dissolved in ether. The ether extract was washed several times with 10% HCl solution and the ether solution of sulfonic acid then neutralized with $Ba(OH)_2$ solution. The ether layer, containing the barium sulfonate, was then separated and dried on the steam bath. The residue was extracted several times with petroleum naphtha (boiling range about 160–235° F.), and the combined extracts were filtered. The filtrate was dried on a drum drier, leaving the barium petroleum sulfonate as a residue, which was found to contain 11.41% barium and 5.61% sulfur.

Example 2

Sulfur-treated barium mahogany sulfonate

100 grams of barium mahogany sulfonate (prepared as described in Example 1), 300 grams of xylene, and 2.8 grams of sulfur were placed in a 3-liter round-bottom flask and heated under reflux for 6 hours. H_2S was evolved during the reaction. The xylene was removed from the reaction product by evaporation on the steam bath and finally under vacuum. The final product was ground to a powder and was found to be more soluble in mineral oil than the original barium sulfonate. It contained 7.62% sulfur.

Example 3

Calcium tetraisobutylphenol sulfonate

296 grams of phenol and 660 grams of tetraisobutylene were placed in a reaction flask together with 1800 cc. of petroleum naphtha (boiling range about 160–235° F.). By means of a dropping funnel, 624 grams of 96% H_2SO_4 was added drop by drop to the stirred mixture, the temperature being maintained below 35° C. After a contact time of 8 hours the spent acid was withdrawn and the mixture recontacted with 300 grams of fresh acid for an additional 8 hour period. 900 cc. of the resulting supernatant layer of alkyl phenol sulfonic acid was neutralized with calcium hydroxide until slightly alkaline to litmus. The mixture was then stirred for 1 hour and a small amount of isopropyl alcohol added to facilitate the separation into two layers. The calcium sulfonate layer was extracted with petroleum naphtha and the naphtha extract was dried over $CaCl_2$ and filtered. The filtrate was dried on a drum drier, yielding 360 grams of a light colored powder, soluble in refined mineral lubricating oils. The calcium tetraisobutylphenol sulfonate was further purified by redissolving in petroleum naphtha, filter-

ing and drying. The purified salt contained 7.79% calcium, indicating that the salt consisted largely of a double salt in which the hydrogen of both the sulfo and hydroxy groups is replaced by the metal.

EXAMPLE 4

Sulfur-treated calcium tetraisobutylphenol sulfonate

20 parts by weight of the calcium double salt of tetraisobutylphenol sulfonic acid (prepared as described in Example 3) was dissolved in 45 parts of refined SAE 20 grade mineral lubricating oil containing 5 parts of a commercial stearyl alcohol. The solution was heated to 110° C. for about 5–10 minutes with 1 part of sulfur, which appeared to react completely during this period. The product was then filtered, giving a concentrate containing about 40% of additive material.

EXAMPLE 5

Bearing corrosion tests

The purpose of the following tests was to determine the corrosion inhibiting effect of adding a small quantity of the products prepared in accordance with the preceding examples to a lubricating oil base.

Base oil A was a solvent extracted paraffinic type mineral lubricating oil of S. A. E. 20 grade, and base oil B was a solvent extracted Mid-Continent paraffinic oil of 52 seconds Saybolt viscosity at 210° F.

The tests were conducted as follows: 500 cc. of the oil to be tested was placed in a glass oxidation tube (13" long and 2⅝" diameter) fitted at the bottom with a ¼" bore air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heated bath so that the oil temperature was maintained at 325° F. during the test. Two quarter sections each of automotive bearings of copper-lead alloy and cadmium-silver alloy of known weight having a total area of 25 sq. cm. for each alloy were attached to opposite sides of a stainless steel rod which was then immersed in the oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. The bearings were washed and weighed at the end of a 16 hour period. The results are shown in the following table. It will be seen that treatment of the metal sulfonates with sulfur in accordance with the present invention rendered them entirely non-corrosive.

Oil	Bearing Weight Loss (Mg./25 sq. cm.)	
	Cu-Pb	Cd-Ag
Base oil A	0	0
Base oil A+2.2% barium mahogany sulfonate (Ex. 1)	422	1,336
Base oil A+2% sulfur-treated barium mahogany sulfonate (Ex. 2)	0	0
Base oil B		
Base oil B+1% calcium double salt of tetraisobutylphenol sulfonic acid (Ex. 3)	18	0
Base oil B+2.5% of 40% concentrate of Sulfur-treated calcium double salt of tetraisobutylphenol sulfonic acid (Ex. 4)	0	0

Although in most instances the additives of the present invention will of themselves impart sufficient improvement to lubricating oils to give very satisfactory results, still greater improvement may often be obtained by employing these addition agents in conjunction with other addi-

tives of the detergent type such as metal soaps, metal phenates, metal alcoholates, metal phenol sulfides, metal organo-phosphates, thiophosphates, phosphites and thiophosphites, metal thiocarbamates, metal xanthates and thioxanthates, and the like.

Thus, for example, the addition agents of our invention may be used in mineral lubricating oil in conjunction with one or more of the following representative materials:

Barium tert.-octyl phenol sulfide
Cobalt tert.-amyl phenol sulfide
Tin salt of wax alkylated phenol sulfide
Magnesium cetyl phenate
Nickel oleate
Barium salt of bis(2,4-diamyl phenol)-4-amyl-phenol dithioether
Zinc salt of salicylic acid sulfide octyl ester
Barium 2-stearoyl-4-amyl phenol sulfide
Aluminum-calcium mixed soap of fatty acid from oxidation of petroleum fractions
Barium octadecylate
Calcium dichlorostearate
Nickel amyl xanthate
Calcium phenyl stearate
Nickel dibutyl dithiocarbamate
Barium dioctyl dithiophosphate
Calcium cetyl phenyl thiophosphate
Zinc methyl cyclohexyl dithiophosphate
Calcium dihexadecyl monothiophosphite
Calcium cetyl phosphate
Zinc diisopropyl salicylate
Aluminum naphthenate
Barium di-tert.-amyl phenol sulfide
Calcium phenate-barium carboxylate of octadecyl salicylic acid
Tin naphthenate

The lubricating oil base stocks 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, 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 to 100, or even higher, viscosity index.

In addition to the 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, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Specific examples of such other agents include dibenzyl disulfide, 2,6-di-tert.-butyl-4-methyl phenol, sulfurized sperm oil, diamyl trisulfide, voltolized sperm oil, polyisobutylene, polymerized lauryl methacrylate, sulfurized wax olefins, and the product of treating a sulfur monochloride diisobutylene reaction product with phenol. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like, may also be employed.

Additives which are particularly desirable as plasticizers and defoaming agents are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol ($C_8H_{17}OH$), lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol ($C_{16}H_{33}OH$), heptadecyl alcohol ($C_{17}H_{35}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol, ($C_{18}H_{37}OH$), and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes, the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc. These assisting agents serve to enhance the detergent and sludge dispersive qualities and aid the solubility of the metal-containing additives and at the same time impart oiliness properties to the lubricating oil compositions.

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.

Since these additives are believed to possess the ability to modify surface activity, they may be employed in asphalts, road oils, waxes, fatty oils of animal or vegetable origin, soaps, and plastics. Similarly, they may be used as modifying agents in natural and synthetic rubber.

The present invention is not to be considered as limited by any of the examples described herein which are given by way of illustration only, but it is to be limited solely by the terms of the appended claims.

We claim:

1. A compounded lubricant comprising a mineral lubricating oil base and at least a corrosion-inhibiting amount of a reaction product of about 0.02 to about 3 atomic proportions of elemental sulfur with one molecular proportion of a metal salt of a sulfonic acid.

2. A lubricant according to claim 1 in which the metal of the metal salt is a metal of group II of the periodic table.

3. A compounded lubricant comprising a mineral lubricating oil base and at least a corrosion-inhibiting amount of a reaction product of about 0.02 to about 3 atomic proportions of elemental sulfur with one molecular proportion of a metal salt of an alkylated phenol sulfonic acid.

4. A compounded lubricant comprising a mineral lubricating oil base and at least a corrosion-inhibiting amount of a reaction product of about 0.02 to about 3 atomic proportions of elemental sulfur with one molecular proportion of a metal salt of petroleum sulfonic acids.

5. A lubricant according to claim 4 in which the metal of the metal salt is a metal of group II of the periodic table.

6. A lubricant according to claim 4 in which the metal of the metal salt is an alkaline earth metal.

7. A compounded lubricant comprising a mineral lubricating oil base and at least a corrosion-inhibiting amount of a product obtained by reacting about 0.1 to about 2.5 atomic proportions of sulfur with one molecular proportion of an alkaline earth metal salt of petroleum sulfonic acid.

8. A lubricant according to claim 7 in which the sulfur and metal salt are reacted in the presence of a hydrocarbon solvent.

9. A compounded lubricant comprising a mineral lubricating oil base and at least a corrosion-inhibiting amount of a product obtained by reacting about equal atomic proportions of barium mahogany sulfonate and elemental sulfur in the presence of xylene maintained at refluxing temperature under normal pressure.

10. A compounded lubricant comprising a mineral lubricating oil and at least a corrosion-inhibiting amount of a product obtained by reaction of sulfur with a mineral oil solution of an alkaline earth metal salt of a sulfonic acid in the proportions of about 0.1 to 2.5 atomic proportions of sulfur to one molecular proportion of sulfonate salt.

11. A compounded lubricant comprising a mineral lubricating oil base and the product obtained

by reacting the calcium double salt of tetraisobutylphenol sulfonic acid with elemental sulfur in the presence of a mineral lubricating oil in such proportions that 0.5 to 1.5 atomic proportions of sulfur are present for each atomic proportion of calcium, the amount of lubricating oil solvent being such that as a result of the reaction a concentrated solution of approximately 40% of reaction product is obtained.

12. As a new composition of matter the reaction product of about 0.02 to about 3 atomic proportions of elemental sulfur with one molecular proportion of a metal salt of a sulfonic acid.

13. As a new composition of matter the reaction product of about 0.02 to about 3 atomic proportions of elemental sulfur with one molecular proportion of a metal salt of a sulfonic acid, the metal of said salt being a metal of group II of the periodic table.

14. As a new composition of matter the reaction product of about 0.02 to about 3 atomic proportions of elemental sulfur with one molecular proportion of a metal salt of petroleum sulfonic acid.

15. As a new composition of matter the product obtained by reacting about 0.1 to about 2.5 atomic proportions of elemental sulfur with one molecular proportion of an alkaline earth metal salt of petroleum sulfonic acid.

16. As a new composition of matter a product obtained by reacting about equal atomic proportions of barium mahogany sulfonate and elemental sulfur in the presence of xylene maintained at a refluxing temperature under normal pressure.

17. The method of preparing an additive for improving the properties of mineral lubricating oils which comprises reacting about 0.1 to about 2.5 atomic proportions of sulfur with one molecular proportion of an alkaline earth metal salt of petroleum sulfonic acid.

18. The method of preparing an additive for improving the properties of mineral lubricating oils which comprises reacting about equal molecular proportions of elemental sulfur and barium mahogany sulfonate in the presence of xylene maintained at refluxing temperature at normal pressure.

19. The method of preparing an additive for improving the properties of mineral lubricating oils which comprises reacting sulfur with a mineral oil solution of an alkaline earth metal salt of a sulfonic acid in the proportions of about 0.1 to 2.5 atomic proportions of sulfur to one molecular proportion of sulfonate salt.

JOHN G. McNAB.
DILWORTH T. ROGERS.

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