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3,242,079

## BASIC METAL-CONTAINING THICKENED OIL COMPOSITIONS

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No Drawing. Filed Apr. 6, 1962, Ser. No. 185,521  
20 Claims. (Cl. 252-33)

This invention relates to thickened mineral oil compositions and to a process for preparing the same. In a more particular sense it relates to homogeneous grease compositions characterized by a high basicity. The compositions of this invention are useful as lubricants and additives in lubricants, asphalts, fuels, cutting oils, caulking compositions, etc.

An undesirable characteristic of lubricating oils is the tendency to become less viscous as the temperature is increased. This viscosity-temperature relationship is expressed in terms of a "viscosity index" which is derived from the viscosity values of the oil at 100° F. and 210° F. The higher the viscosity index, the less susceptibility of the oil to viscosity changes with temperature. Another undesirable characteristic of lubricating oils is the tendency to deteriorate in service. The products of deterioration are corrosive to metals and tend to form deposits in the equipment being lubricated.

A common practice to obviate these undesirable characteristics is to incorporate into the lubricating oil chemical additives such as viscosity index improving agents, oxidation- and corrosion-inhibiting agents, and detergents. The viscosity index additives are illustrated by the high molecular weight olefin polymers and polyacrylates. Unfortunately, their effectiveness is associated with only a relatively narrow range of high molecular weights. The manufacture of the polymers having molecular weights within such narrow range is costly. Another drawback of these additives is that the polymers, by their very nature, are susceptible to degradation under high temperature and pressure service conditions. They tend to lose their effectiveness after a period of use.

The detergent additives useful for preventing the formation of harmful deposits are illustrated by the metal salts of oil-soluble acids such as sulfonic acids, organic phosphorus acids, and carboxylic acids. The so-called basic metal salts, i.e., those in which the metal is present in a stoichiometrically greater amount than the organic acid radical, are especially effective because of their additional ability to counteract the corrosive, acidic products of oil degradation. In general, the higher the basicity, the more effective the metal salt as a lubricant additive.

A number of processes are known for preparing the highly basic metal salts and incorporating them into fluid lubricating compositions. However, attempts to incorporate highly basic metal salts into greases have not been entirely successful. Such attempts either have failed to impart a high basicity to the grease or have resulted in a non-homogeneous grease of poor quality.

Accordingly it is an object of this invention to provide a grease composition.

It is also an object of this invention to provide a grease composition having a high basicity.

It is also an object of this invention to provide a grease composition resistant to deterioration and the formation of harmful deterioration products.

It is also an object of this invention to provide a relatively homogeneous grease composition.

It is further an object of this invention to provide a thickened homogeneous mineral oil composition capable of improving the viscosity index properties of lubricating oils.

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It is further an object of this invention to provide a lubricant additive.

It is also an object of this invention to provide a concentrate of a lubricant additive.

It is further an object of this invention to provide novel compositions of matter.

It is further an object of this invention to provide a method for inhibiting the corrosion of a metal surface by depositing on said surface a film of a grease composition.

These and other objects are attained in accordance with this invention by providing a process for preparing a homogeneous grease composition comprising mixing a fluid mineral oil solution containing from about 10% to about 70% of a carbonated, basic alkaline earth metal salt of an acid having at least about 12 aliphatic carbon atoms selected from the class consisting of sulfonic acids and carboxylic acids, said salt having a metal ratio of at least about 4.5, and from about 1% to about 80%, based on said metal salt, of an active hydrogen compound selected from the class consisting of lower aliphatic carboxylic acids, water, and water-alcohol mixtures at a temperature between about 25° C. and the reflux temperature.

The term "metal ratio" is used herein to designate the ratio of the total chemical equivalents of the metal in the metal salt to the chemical equivalents of the metal which is in the form of a normal salt, i.e., a neutral salt of the organic acid. To illustrate, a metal salt containing 5 equivalents of the metal per equivalent of the organic acid radical has a metal ratio of 5; and a neutral metal salt has a metal ratio of 1.

The process of this invention can be effected simply by homogenizing, e.g., by vigorous agitation or mixing, the ingredients in the appropriate proportions until the reaction mixture thickens to a grease. In most instances, a period of at least one hour of mixing is desirable. The volatile components may be removed from the product by evaporation or distillation. The temperature at which the grease-forming process is carried out is preferably the reflux temperature or a temperature slightly below the reflux temperature. It may be as low as 25° C. and seldom exceeds 150° C.

The presence of an active hydrogen compound described above is critical to the formation of the grease product. It may be water or a water-alcohol mixture or a lower aliphatic carboxylic acid. The alcohols useful herein include aliphatic, cycloaliphatic, and aromatically substituted aliphatic alcohols. Those having less than about 12 carbon atoms are especially useful and the lower alcohols, i.e., those having less than about 8 carbon atoms are preferred for reasons of economy and effectiveness in the process. They are illustrated by methanol, ethanol, isopropanol, n-propanol, isobutanol, secondary butanol, cyclopentanol, cyclohexanol, 4-methyl-cyclohexanol, isooctanol, dodecanol, benzyl alcohol, cinnamyl alcohol, 2-cyclopentyl-propanol, chloro hexanol, bromooctanol, monomethyl ether of ethylene glycol, diethylene glycol, ethylene glycol, trimethylene glycol, hexamethylene glycol, triethylene glycol, 1,4-butanediol, 1,4-cyclohexanediol, glycerol, pentaerythritol, and the like.

The use of a mixture of water and one or more of the alcohols is especially effective in facilitating the formation of the grease product. It often reduces the length of the time required for the process. A very effective combination is a mixture of an alcohol (or alcohols) and water in a weight ratio within the range from 0.5:1 to 3:1, respectively.

The lower aliphatic carboxylic acids are those containing less than about 8 carbon atoms in the molecule. They include, for example, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, isovaleric acid, isobutyric

acid, caproic acid, heptioic acid, caprylic acid, chloroacetic acid, dichloroacetic acid, and trichloroacetic acid. Of these, formic acid, acetic acid, and propionic acid are preferred. The anhydrides of these acids likewise are useful and for the purposes of the specifications and claims of this invention the term "acid" thus includes both the acid and the anhydride of the acid.

The concentration of the active hydrogen compound in the process is usually within the range from about 1% to 80% based upon the weight of the carbonated, basic metal salt. The concentration is preferably at least about 10% and usually less than 60% by weight of the metal salt. On the other hand, higher concentrations, i.e., above 80%, may be used but the excess appears not to have any additional beneficial effects and ordinarily is not necessary.

The carbonated, basic alkaline earth metal salts useful in the above process are the salts of magnesium, calcium, strontium, and barium with a long chain sulfonic acid or carboxylic acid. The acid should contain at least about 12 aliphatic carbon atoms in the molecule. The sulfonic acids include the aliphatic and the aromatic sulfonic acids. They are illustrated by petroleum sulfonic acids or the acids obtained by treating an alkylated aromatic hydrocarbon with a sulfonating agent, e.g., chlorosulfonic acid, sulfur trioxide, oleum, sulfuric acid, or sulfur dioxide and chlorine. The sulfonic acids obtained by sulfonating the alkylated benzene, naphthylene, phenol, phenol sulfide, or diphenyl oxide are especially useful.

Specific examples of the sulfonic acids are mahogany acid, mono-wax (eicosane)-substituted naphthylene sulfonic acid, dodecylbenzene sulfonic acid, didodecylbenzene sulfonic acid, dinonylbenzene sulfonic acid, octadecyl-diphenyl ether sulfonic acid, octadecyl-diphenyl amine sulfonic acid, cetyl-chlorobenzene sulfonic acid, bis-cetylphenyl disulfide sulfonic acid, cetoxy-caprylbenzene sulfonic acid, dilauryl beta-naphthalene sulfonic acid, the sulfonic acid derived by the treatment of polyisobutene having a molecular weight of 1500 with chloro sulfonic acid, nitronaphthylene sulfonic acid, paraffin wax sulfonic acid, cetyl-cyclopentane sulfonic acid, lauryl-cyclohexane sulfonic acid, and polyethylene (molecular weight of 750) sulfonic acid, etc. The carboxylic acids likewise may be aliphatic or aromatic acids. They are exemplified by palmitic acid, stearic acid, myristic acid, oleic acid, linoleic acid, behenic acid, hexatriacontanoic acid, tetrapropylene-substituted glutaric acid, polyisobutene (molecular weight of 5000)-substituted succinic acid, polypropylene (molecular weight of 10,000)-substituted succinic acid, octadecyl-substituted adipic acid, chlorostearic acid, 9-methylstearic acid, dichlorostearic acid, stearylbenzoic acid, poly wax (eicosane)-substituted naphthoic acid, dilauryl-decahydronaphthylene carboxylic acid, didodecyl-tetralin carboxylic acid, dioctyl-cyclohexane carboxylic acid, and the anhydrides of such acids.

An important aspect of the carbonated, basic alkaline earth metal salts of the above-illustrated oil-soluble acids is that they have a metal ratio of at least about 4.5. The necessity of this high metal ratio is predicated upon the discovery that the use of a salt having a metal ratio less than 4.5 in the above process will not result in a product having the thickness of a grease. On the other hand, the use of salts having a metal ratio between about 8 and 20 has been found to be most advantageous, although salts having still higher metal ratios likewise are effective.

A convenient process for preparing the metal salts comprises carbonating a substantially anhydrous mixture of the acid with at least about 4.5 chemical equivalents of an alkaline earth metal base per equivalent of the acid in the presence of a promoting agent. The metal base may be an alkaline earth metal oxide, hydroxide, bicarbonate, sulfide, mercaptide, hydride, alcoholate, or

phenate. It is preferably an oxide, alcoholate, or hydroxide of barium or calcium. The carbonation is carried out in a solvent which is preferably mineral oil. The solvent may be n-hexane, naphtha, n-decane, dodecane, benzene, toluene, xylene, or any other fluid hydrocarbon.

The promoting agent is preferably an alcohol or a phenol; it may be a mercaptan, amine, aci-nitro compound, or an enolic compound. The alcohols and phenols useful as the promoting agent include, for example, methanol, ethanol, isopropanol, cyclohexanol, decanol, dodecanol, behenyl alcohol, ethylene glycol, diethylene glycol triethylene glycol, monomethyl ether of ethylene glycol, trimethylene glycol, hexamethylene glycol, glycerol, pentaerythritol, benzyl alcohol, phenylethyl alcohol, phenol, naphthol, cresol, catechol, p-tert-butylphenol, m-polyisobutene (molecular weight of 350)-substituted phenol, o,p-didodecylphenol, alpha-hexyl-beta-naphthol, m-cyclohexyl-phenol, 4,4' - methylene-bisphenol, 2,2' - methylene-4,4'-dioctyl bisphenol, etc. Other compounds useful as the promoting agent are illustrated by acetoacetate, acetylacetone, acetamide, ethanolamine, diethanolamine, triethanolamine, nitro-methane, nitro-propane, nitro-decane, nitro-benzene, nitro-toluene, methylamine, dimethylamine, aniline, phenylenediamine, N,N'-dimethyl phenylenediamine, toluidine, cyclohexylamine, N-methyl decylamine, naphthylamine, o-chlorophenol, m-nitrophenol, o-methoxy-phenol, thiophenol, methyl mercaptan, dodecyl mercaptan, isooctyl mercaptan, benzyl mercaptan, etc.

It will be noted that upon mixing with the alkaline earth metal base, the sulfonic or carboxylic acid forms a metal salt so that the process mixture before carbonation contains a metal salt of the acid and a large excess of the metal base. Such a mixture is heterogeneous primarily because of the presence of the large excess of the insoluble metal base. As carbonation proceeds, the metal base becomes solubilized in the organic phase and the carbonated product eventually becomes a homogeneous composition containing an unusually large amount of the metal. The mechanism of the formation of the homogeneous product is not fully understood. It is believed, however, that carbonation converts the excess metal base to a carbonate or bicarbonate which forms with the metal salt of the oil-soluble acid a homogeneous complex. The complex is readily soluble in hydrocarbon solvents such as benzene, xylene, and mineral oil. However, it is not necessary for all of the metal base present in the process mixture to be so converted by carbonation to produce a soluble, homogeneous product. In many instances a homogeneous product is obtained when as little as 75% of the excess metal base is carbonated. For the sake of convenient reference in the specification and the claims of this invention, the term "carbonated, basic alkaline earth metal salt" of the oil-soluble acid designates the homogeneous, carbonated product without specific reference to the degree of conversion of the excess metal base by carbonation.

The formation of the carbonated, basic alkaline earth metal salt having the high metal ratio of at least about 4.5 requires the presence in the carbonation step of a promoting agent such as is described previously. The amount of the promoting agent to be used is best defined in terms of its chemical equivalents per equivalent of the long chain sulfonic or carboxylic acid used. The amount may be as little as 0.1 equivalent or as much as 10 equivalents or even more per equivalent of the acid. The preferred amount is within the range from 0.25 to 5 equivalents per equivalent of the acid. It will be noted that the equivalent weight of the promoting agent is based upon the number of the functional radicals in the molecule. To illustrate, the equivalent weight of an alcohol is based upon the number of the alcoholic radicals in the molecule; that of a phenol is based upon the number of the hydroxyl radicals in the molecule; that

of an amine is based upon the number of the amino radicals in the molecule; etc. Thus, methanol has one equivalent per mole; ethylene glycol has two equivalents per mole; a bis-phenol has two equivalents per mole; phenylene-diamine has two equivalents per mole; nitro-propane has one equivalent per mole; acetylacetone has one equivalent per mole; etc.

The carbonation temperature depends to a large measure upon the promoting agent used. When a phenol is used as the promoting agent the temperature usually ranges from about 80° C. to 300° C. and preferably from 100° C. to 200° C. When an alcohol or a mercaptan is used as the promoting agent the carbonation temperature usually will not exceed the reflux temperature of the reaction mixture and preferably will not exceed 100° C.

After carbonation, the promoting agent, if it is a volatile substance, may be removed from the product by distillation. If the promoting agent is a non-volatile substance it is usually allowed to remain in the product. The methods for preparing the carbonated, basic metal salts include those described in, e.g., U.S. Patents 2,616,905, 2,616,924, 2,695,910, 2,971,014, and copending applications, Serial Nos. 545,550 filed on November 7, 1955 now Patent No. 3,027,325 and 585,603, filed on October 10, 1959 now Patent No. 3,133,944.

As indicated previously, the process of this invention for the preparation of the grease comprises treating a mineral oil solution of the carbonated, basic alkaline earth metal salt with an active hydrogen compound. The mineral oil solution of the carbonated, basic alkaline earth metal salt can be obtained simply by dissolving the metal salt in a mineral oil. If the metal salt is prepared in the presence of a solvent other than a mineral oil, the solvent is removed by distillation after the metal salt is dissolved in a mineral oil. An important aspect in the formation of the grease by the process of this invention is that the mineral oil solution of the metal salt be free from insoluble contaminants. Thus, if any contaminants are present in the mineral oil solution as a result of, e.g., insufficient carbonation of the alkaline earth metal base used in preparing the carbonated basic metal salt, the mineral oil solution must then be filtered or centrifuged before it is used in the process of this invention. The necessity of removing the insoluble contaminants is predicated upon the discovery that unless they are so removed, a grease can not be obtained or if obtained, it will have neither the degree of homogeneity nor the other desirable characteristics. In this regard it will be noted, therefore, that an essence of the present invention includes the separate steps of the preparation of a homogeneous, carbonated, basic alkaline earth metal salt having a high metal ratio and the preparation of a grease from a mineral oil solution of such a metal salt by the treatment with an active hydrogen compound.

The concentration of the carbonated, basic salt in the mineral oil solution should be at least about 10% by weight. If the concentration is below about 10%, a grease usually can not be formed by the process. Also, there should be a sufficient quantity of mineral oil in the solution so that the initial mixture of the grease-forming process is fluid. Ordinarily the solution should contain at least about 30% by weight of a mineral oil. The mineral oil useful herein is preferably one having a viscosity value ranging from 50 SUS (Saybolt Universal Seconds) at 100° F. to 500 SUS at 210° F. Especially useful is a mineral oil from SAE 5 to SAE 120 grade. The sources of the mineral oils are not critical.

The following examples illustrate the preparation of the carbonated, basic metal salts useful in the process of this invention.

#### Example 1

To a mixture of 3245 grams (12.5 equivalents) of barium oil solution of barium petroleum sulfonate (sulfate ash of 7.6%), 32.5 parts of octyl phenol, 197 parts of

water, there is added 73 parts of barium oxide within a period of 30 minutes at 57°–84° C. The mixture is heated at 100° C. for 1 hour to remove substantially all water and blown with 75 parts of carbon dioxide at 133°–170° C. within a period of 3 hours. A mixture of 1000 grams of the above carbonated intermediate product and 121.8 parts of octyl phenol and 234 parts of barium hydroxide is heated at 100° C. and then at 150° C. for one hour. The mixture is then blown with carbon dioxide at 150° C. for one hour at a rate of 3 cubic ft. per hour. The carbonated product is filtered and the filtrate is found to have a sulfate ash content of 39.8 and a metal ratio of 9.3.

#### Example 2

To a mixture of 3245 grams (12.5 equivalents) of barium petroleum sulfonate, 1460 grams (7.5 equivalents) of heptyl phenol, and 2100 grams of water in 8045 grams of mineral oil there is added at 180° F., 7400 grams (96.5 equivalents) of barium oxide. The addition of barium oxide caused the temperature to rise to 290° F. which temperature is maintained until all of the water has been distilled. The mixture then is blown with carbon dioxide until it is substantially neutral. The product is diluted with 5695 grams of mineral oil and filtered. The filtrate is found to have a barium sulfate ash content of 30.5% and a metal ratio of 8.1.

#### Example 3

A mixture of 1285 grams (1.0 equivalent) of 40 percent barium petroleum sulfonate and 500 ml. (12.5 equivalents) of methanol is stirred at 55–60° C. while 301 grams (3.9 equivalents) of barium oxide is added portionwise over a period of one hour. The mixture is stirred an additional two hours at 45–55° C., then treated with carbon dioxide at 55–65° C. for two hours. The resulting mixture is freed of methanol by heating to 150° C. The residue is filtered through a siliceous filter aid, the clear, brown filtrate showing the analyses: sulfate ash, 33.2%; neut. No. slightly acid; metal ratio, 4.7.

#### Example 4

A solution of 1928 grams (1.5 equivalents) of 40 percent barium petroleum sulfonate in 1004 grams of oil and 188 ml. (4.7 equivalents) of methanol is prepared and heated to 40° C. Carbon dioxide is bubbled into this solution and 796 grams (10.4 equivalents) of barium oxide is added portionwise over a period of two hours. The temperature is maintained between 40° C. and 70° C. throughout and when all the barium oxide has been added the carbon dioxide-treatment is continued for an additional four hours. The resulting mixture is then heated to 150° C. and held at this temperature for 30 minutes to remove any volatile material. The residue is filtered, yielding a clear, brown filtrate having the following analyses: sulfate ash, 32.5%; neut. No. 1.2 (basic); metal ratio, 7.2.

#### Example 5

A stirred mixture of 57 grams (0.4 equivalent) of nonyl alcohol and 301 grams (3.9 equivalents) of barium oxide is heated at 150–175° C. for an hour, then cooled to 80° C. whereupon 400 grams (12.5 equivalents) of methanol is added. The resultant mixture is stirred at 70–75° C. for 30 minutes, then treated with 1285 grams (1.0 equivalent) of 40 percent barium petroleum sulfonate. This mixture is stirred at reflux temperature for an hour, then treated with carbon dioxide at 60–70° C. for two hours. The mixture then is heated to 160° C./18 mm. and filtered. The filtrate is a clear, brown oil having the following analyses: sulfate ash, 32.5%; neut. No. nil; metal ratio, 4.7.

#### Example 6

A mixture of 574 grams (0.5 equivalent) of 40 percent barium petroleum sulfonate, 98 grams (1.0 equivalent) of

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furfuryl alcohol, and 762 grams of mineral oil is heated with stirring at 100° C. for an hour, then treated portionwise over a 15-minute period with 230 grams (3.0 equivalents) of barium oxide. During this latter period the temperature rises to 120° C. (because of the exothermic nature of the reaction of barium oxide and the alcohol); the mixture then is heated at 150–160° C. for an hour, and treated subsequently at this temperature for 1.5 hours with carbon dioxide. The material is concentrated by heating to a final temperature of 150° C./10 mm. then filtered to yield a clear, oil-soluble filtrate having the following analyses: sulfate ash, 21.4%; neut. No. 2.6 (basic); metal ratio, 6.1.

#### Example 7

To a mixture of 1145 grams of a mineral oil solution of a 40% solution of barium mahogany sulfonate (one equivalent) and 100 grams of methyl alcohol at 55° C. there is added 220 grams of barium oxide while the mixture is being blown with carbon dioxide at a rate of 2–3 cubic feet per hour. To this mixture there is added an additional 78 grams of methyl alcohol and then 460 grams of barium oxide while the mixture is being blown with carbon dioxide. The carbonated product is heated to 150° C. for one hour and filtered. The filtrate is found to have a barium sulfate ash content of 53.8 percent and a metal ratio of 8.9.

#### Example 8

A carbonated basic metal salt is prepared in accordance with the procedure of Example 7 except that a total of 16 equivalents of barium oxide is used per equivalent of the barium mahogany sulfonate used. The product is found to have a metal ratio of 13.4.

#### Example 9

A mixture of 520 parts (by weight) of a mineral oil, 480 parts of a sodium petroleum sulfonate (molecular weight of 480), and 84 parts of water is heated at 100° C. for 4 hours. The mixture is then heated with 86 parts of a 76% aqueous solution of calcium chloride and 72 parts of lime (90% purity) at 100° C. for 2 hours, dehydrated by heating to a water content of less than 0.5%, cooled to 50° C., mixed with 130 parts of methyl alcohol, and then blown with carbon dioxide at 50° C. until substantially neutral. The mixture is then heated to 150° C. to distill off methyl alcohol and water and the resulting oil solution of the basic calcium sulfonate filtered. The filtrate is found to have a calcium sulfate ash content of 16% and a metal ratio of 2.5. A mixture of 1305 grams of the above carbonated calcium sulfonate, 930 grams of mineral oil, 220 grams of methyl alcohol, 72 grams of isobutyl alcohol, and 38 grams of amyl alcohol is prepared, heated to 35° C., and subjected to the following operating cycle 4 times: mixing with 143 grams of 90% calcium hydroxide and treating the mixture with carbon dioxide until it has a base number of 32–39. The resulting product is then heated to 155° C. during a period of 9 hours to remove the alcohols and then filtered through a siliceous filter-aid at this temperature. The filtrate has a calcium sulfate ash content of 39.5%, and a metal ratio of 12.2.

#### Example 10

A basic metal salt is prepared by the procedure described in Example 9 except that the slightly basic calcium sulfonate having a metal ratio of 2.5 is replaced with a mixture of that calcium sulfonate (280 parts by weight) and tall oil acids (970 parts by weight, having an equivalent weight of 340) and that the total amount of calcium hydroxide used is 930 parts by weight. The resulting highly basic metal salt of the process has a calcium sulfate ash content of 48%, a metal ratio of 7.7, and an oil content of 31%.

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#### Example 11

A highly basic metal salt is prepared by the procedure of Example 10 except that the slightly basic calcium sulfonate starting material having a metal ratio of 2.5 is replaced with tall oil acids (1250 parts by weight, having an equivalent weight of 340) and the total amount of calcium hydroxide used is 772 parts by weight. The resulting highly basic metal salt has a metal ratio of 5.2, a calcium sulfate ash content of 41%, and an oil content of 33%.

#### Example 12

A highly basic metal salt is prepared by the procedure of Example 10 except that the slightly basic calcium sulfonate starting material is replaced with a mixture of that basic calcium sulfonate (555 parts by weight) and tall oil acids (694 parts by weight having an equivalent weight of 340) and the amount of calcium hydroxide used is 772 parts by weight. The resulting metal salt has a metal ratio of 7.9, a calcium sulfate ash content of 45%, and an oil content of 32%.

#### Example 13

A basic metal salt is prepared by the process of Example 9 except that the amount of the slightly basic calcium sulfonate used is 1672 parts and the amount of the calcium hydroxide used is 704 parts. The resulting highly basic metal salt has a metal ratio of 12.2, and a calcium sulfate ash content of 40%.

#### Example 14

A highly basic metal salt is prepared by the procedure of Example 13 except that the slightly basic calcium sulfonate starting material has a metal ratio of 1.6 and the amount of this calcium sulfonate used is 1050 parts (by weight) and that the total amount of lime used is 630 parts. The resulting metal salt has a calcium sulfate ash content of 40%, a metal ratio of 16 and an oil content of 35%.

The following examples illustrate the process of this invention for the preparation of the homogeneous grease compositions: (the penetration values reported herein are obtained by the ASTM D-217 procedure at 77° F.).

#### Example A

To 733 grams of the carbonated, basic metal salt of Example 7, there is added 179 grams of acetic acid and 275 grams of a mineral oil having a viscosity of 2000 SUS at 100° F. at 90° C. in 1.5 hours with vigorous agitation. The mixture is then homogenized at 150° C. for 2 hours and the resulting product is a grease.

#### Example B

A mixture of 960 grams of the carbonated, basic metal salt of Example 8, 256 grams of acetic acid, and 300 grams of a mineral oil having a viscosity of 2000 SUS at 100° F. is homogenized by vigorous stirring at 150° C. for 2 hours. The product is a grease.

#### Example C

To 150 parts of the carbonated, basic metal salt of Example 10 there is added 75 parts of a mineral oil having a viscosity of 2000 SUS at 100° F. and 50 parts of acetic acid. The resulting mixture is homogenized by vigorous agitation at 100° C. for 6 hours, heated to 150° C. in 3 hours, diluted with 75 parts of the mineral oil, and then heated at 130°–145° C. for 4 hours whereupon the volatile components are removed. The residue is a grease.

#### Example D

A mixture of 150 parts of the carbonated basic metal salt of Example 11, 45 parts of acetic acid, and 100 parts of a mineral oil having a viscosity of 2000 SUS at 100° F. is homogenized at 100° C. for 5 hours and then at 145°–115° C. for 9.5 hours. The resulting product is a grease having a penetration value of 229.

*Example E*

A mixture of 45 parts of acetic acid and 50 parts of a mineral oil having a viscosity of 2000 SUS at 100° F. is added to 150 parts of the carbonated, basic metal salt of Example 12 in 5 hours at 100° C. The mixture is homogenized at this temperature for 2.5 hours, heated to 150° C. in 2.5 hours, diluted with 50 parts of the mineral oil and homogenized again for 4 hours at 140°–197° C. The resulting product is a grease having a penetration value of 260.

*Example F*

A grease is prepared by the procedure of Example E except that the temperature of the homogenation process is maintained between 138°–145° C. The grease has a penetration value of 343.

*Example G*

A mixture of 150 parts of the carbonated, basic metal salt of Example 12, 15 parts of methyl alcohol, 10.5 parts of p-pentyl alcohol, and 45 parts of water is homogenized at reflux temperature (74° C.) for 5 hours. It is then heated and homogenized at 148° C. for 8.8 hours whereupon the volatile components are removed. The product is a grease having a dropping point above 500° F. and a penetration value of 333.

*Example H*

A mixture of 150 parts of the carbonated, basic metal salt of Example 9, 15 parts of methyl alcohol, 10.5 parts of p-pentyl alcohol, and 45 parts of water is heated under reflux conditions at 71°–74° C. for 13 hours. The mixture solidifies. It is then heated to 144° C. in 6 hours, diluted with 126 parts of a mineral oil having a viscosity of 2000 SUS at 100° F. and the mixture heated at 144° C. for 4.5 hours. The product is a grease having a penetration value of 257.

*Example I*

A mixture of 200 parts of the carbonated, basic metal salt of Example 9, 16 parts of methyl alcohol, 8 parts of p-pentyl alcohol, and 8 parts of water is homogenized at 70°–72° C. (reflux) for 5 hours, in an open vessel to 133° C. in 3 hours, and then at 133° C. for 1 hour. The mixture is allowed to cool to room temperature and a grease is obtained which has a penetration value of 255.

*Example J*

A mixture of 2000 parts of the slightly basic calcium sulfonate having a metal ratio of 2.5 (prepared as described in Example 9), 160 parts of methyl alcohol, 80 parts of p-pentyl alcohol, and 80 parts of water is homogenized at 57°–66° C. for 96 hours and then at 150° C. for 2 hours. A grease is not obtained. This demonstrates the criticality of the metal ratio of the carbonated basic metal salt used in the process and the importance of using such a carbonated basic metal salt which has a metal ratio greater than 4.5.

*Example K*

A mixture of the slightly basic calcium sulfonate having a metal ratio of 2.5 (167 parts, prepared as described in Example 9), mineral oil (80 parts), calcium hydroxide (70 parts), methyl alcohol (29 parts), isobutyl alcohol (94 parts), amyl alcohol (50 parts), and water (18 parts) is treated with carbon dioxide in a manner similar to that of Example 9 and homogenized in a manner similar to that of Example I. The mixture shows no tendency to form a grease.

The greases prepared by the process of this invention are characterized by homogeneity and stability to air, heat, and moisture. They are also characterized by non-corrosiveness, detergency, and load-carrying properties. They may vary in consistency and hardness from the so-called number 0 grade to number 6 grade, the former

designating greases having a penetration value of 355–385 and the latter designating greases having a penetration value of 85–115 (according to the ASTM D-217 procedure at 77° F. Another desirable characteristic of the greases is a relatively high dropping point (i.e., the temperature at which the grease liquefies) which permits the use of the greases under high temperature service conditions. In most instances, the greases of this invention have a dropping point above about 400° F.; for example, the grease prepared according to Example I has been found to have a dropping point above 500° F.

The stability of the greases against oxidative degradation is measured by a test corresponding to the procedure of ASTM D 942–50. This test consists of placing five 4-gram samples of the grease in a bomb, adjusting the internal pressure of the bomb with oxygen and maintaining the pressure at 110 p.s.i., placing the bomb in a constant temperature bath at 210° F. for 2 hours, and measuring the pressure loss in the bomb at the end of that period. The pressure loss measures the oxygen consumption and therefore measures the extent of oxidation; i.e., a smaller pressure loss indicates a higher oxidation stability of the grease. By this test a grease prepared according to the procedure of Example I shows a pressure drop of 5 p.s.i. whereas a representative commercially available grease may show a pressure drop of as much as 10 p.s.i.

The load-carrying properties of the greases are measured by the Four Ball extreme pressure test. In this test four steel balls are arranged in a tetrahedron, the top ball is made to rotate against the three bottom balls and the points of contact are lubricated by the test grease. The load upon the steel balls is increased until welding of the balls occurs. This load is reported as the "weld point" and the higher its value the better the load-carrying characteristics of the grease. By this test a grease prepared according to the procedure of Example I is found to have a weld point about 800 kilograms.

Another test measuring the load-carrying characteristics of the greases is the Timken OK Load test (ASTM bulletin No. 181, April 1, 1952). In this test the load is measured at which the rupture of a lubricant film between the rotating cup and a stationary block occurs, and at which the surface distress of the stationary block appears. The higher the load, the better the load-carrying characteristics. By this test a grease prepared by the procedure of Example I is found to withstand a load of at least 45 pounds.

The anti-corrosion characteristics of the greases are measured by the Salt-Fog Corrosion test (ASTM Procedure designation B117–57T). In this test a steel panel, coated with the grease at a thickness of 1000 milligrams per square foot, is suspended in a Salt Fog cabinet and a 5% sodium chloride solution is sprayed onto the panel at 100° F. for 24 hours. By this test an uncoated panel is corroded over the entire surface at the end of 24 hours whereas a panel coated with a grease prepared by the procedure of Example I shows no corrosion at the end of 166 hours.

The ability of the grease to withstand prolonged use under severe conditions is shown in a comparison of the penetration values measured before and after working of the grease according to ASTM procedure E217–52T. The working consists essentially of placing the grease in a cylinder and operating a piston for 100,000 strokes at 77° F. A grease prepared according to the procedure of Example I shows penetration values of 322 and 337 respectively before and after working. A representative commercially available premium grade grease shows a change of the penetration value from 293 to 355.

The stability of the grease against deterioration by moisture or water is shown also by the penetration value of 338 for the above-identified grease after it is mixed with 10% by its weight of water and the mixture is "worked" for 100,000 strokes at 77° F.

The thickened mineral oil compositions of this invention are useful as additives in hydrocarbon oil compositions to improve their viscosity index values. When used for this purpose they are usually present in a hydrocarbon oil at concentrations within the range from about 1% to about 30% by weight. The viscosity index improving properties of the thickened mineral oil compositions of this invention are illustrated by the finding that the addition of 19 parts (by weight) of the product of Example I to 81 parts of an SAE 10 mineral oil increases the viscosity index of the oil from 104 to 120.

A portion of the unclaimed subject matter disclosed herein and relating to the metal salts of the substituted succinic acids is disclosed and claimed in co-pending application Ser. No. 395,031, filed September 8, 1964. A portion of the subject matter disclosed and claimed herein and relating to the inhibition of corrosion of metal surfaces is disclosed and claimed in co-pending application Ser. No. 297,701, filed July 5, 1963, now abandoned, which is a continuation-in-part of the present application.

What is claimed is:

1. A homogeneous grease composition prepared by the process comprising mixing a fluid mineral oil solution containing from about 10% to about 70% of a carbonated, basic alkaline earth metal salt of an acid having at least about 12 aliphatic carbon atoms and selected from the class consisting of sulfonic acids and carboxylic acids, said salt having a metal ratio of from about 4.5 to 20 and from about 1% to about 80%, based on said metal salt, of an active hydrogen compound selected from the class consisting of lower aliphatic carboxylic acids, water, and water-alcohol mixture having a weight ratio of water:alcohol from about 1:0.5 to 1:3 at a temperature between about 25° C. and about 200° C.

2. The grease composition of claim 1 wherein the carbonated, basic alkaline earth metal salt is a salt of a sulfonic acid.

3. The grease composition of claim 1 wherein the carbonated, basic alkaline earth metal salt is a salt of a carboxylic acid.

4. The grease composition of claim 1 wherein the carbonated, basic alkaline earth metal salt is a calcium salt.

5. The grease composition of claim 1 wherein the carbonated, basic alkaline earth metal salt is a mixture of salts of a sulfonic acid and a carboxylic acid having a weight ratio of the sulfonic acid salt:carboxylic acid salt from about 1:1 to 1:4.

6. A homogeneous grease composition prepared by the process comprising mixing a fluid mineral oil solution containing from about 10% to about 70% of a carbonated basic calcium salt of an oil-soluble sulfonic acid having a metal ratio from about 4.5 to 20 and from about 5% to about 60%, based on said calcium salt, of acetic acid at a temperature between about 25° C. and about 200° C.

7. A homogeneous grease composition prepared by the process comprising mixing a fluid mineral oil solution containing from about 10% to about 70% of a carbonated, basic calcium salt of a carboxylic acid having at least about 12 aliphatic carbon atoms and having a metal ratio of from about 4.5 to 20 and from about 1% to about 80%, based on said metal salt, of acetic acid at a temperature between about 25° C. and about 200° C.

8. A homogeneous grease composition prepared by the process comprising mixing a fluid mineral oil solution containing from about 10% to about 70% of a carbonated, basic calcium salt of an oil-soluble sulfonic acid having a metal ratio of from about 4.5 to 20 and from about 1% to about 80%, based on said calcium salt, of a water-alcohol mixture having a weight ratio of water:alcohol from about 1:0.5 to 1:3 at a temperature between about 25° C. and about 200° C.

9. A homogeneous grease composition prepared by the process comprising mixing a fluid mineral oil solution containing from about 10% to about 70% of a carbonated, basic calcium salt of a carboxylic acid having at least about 12 aliphatic carbon atoms and having a metal ratio of from about 4.5 to 20 and from about 1% to about 80%, based on said calcium salt, of a water-alcohol mixture having a weight ratio of water:alcohol from about 1:0.5 to 1:3 at a temperature between about 25° C. and about 200° C.

10. A homogeneous grease composition prepared by the process comprising mixing a fluid mineral oil solution containing from about 10% to about 70% of a carbonated, basic calcium sulfonate having a metal ratio of from about 4.5 to 20 prepared by carbonating a mixture comprising an oil-soluble calcium sulfonate and calcium oxide in the presence of an alcoholic promoting agent, and from about 1% to about 80%, based on said carbonated, basic calcium sulfonate, of a water-alcohol mixture having a weight ratio of water:alcohol from about 1:0.5 to 1:3 comprising 3 parts of an alcohol and 1 part of water at a temperature between about 25° C. and about 200° C.

11. The grease composition of claim 10 wherein the carbonated, basic calcium sulfonate has a metal ratio of at least about 8.

12. The grease composition of claim 10 wherein the alcohol in said water-alcohol mixture is a lower alcohol having less than about 8 carbon atoms.

13. A homogeneous grease composition prepared by the process comprising mixing a fluid mineral oil solution containing from about 30% to about 70% of a carbonated, basic calcium sulfonate having a metal ratio of about 12, and from about 1% to about 80%, based on said sulfonate, of a water-alcohol mixture consisting of 2 parts of methyl alcohol, 1 part of pentyl alcohol, and 1 part of water at a temperature between about 50° C. and about 200° C.

14. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion, at least about 1% by weight, of the product of claim 1.

15. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion, at least about 1% by weight, of the product of claim 13.

16. A method for inhibiting the corrosion of a metal surface which comprises depositing on said surface a film of a grease composition prepared by the process comprising mixing at a temperature between about 25° C. and about 200° C., a fluid mineral oil solution containing from about 10% to about 70% of a carbonated, basic alkaline earth metal salt of an acid having at least about 12 aliphatic carbon atoms selected from the class consisting of sulfonic acids and carboxylic acids, said salt having a metal ratio of from about 4.5 to 20 and from about 1% to about 80%, based on said metal salt, of an active hydrogen compound selected from the class consisting of lower aliphatic carboxylic acids, water, and an aqueous alcohol having an alcohol content up to about 80% by weight.

17. The method of claim 16 characterized further in that the carbonated, basic alkaline earth metal salt is a salt of a sulfonic acid.

18. The method of claim 16 characterized further in that the carbonated, basic alkaline earth metal salt is a salt of a carboxylic acid.

19. The method of claim 16 characterized further in that the carbonated, basic alkaline earth metal salt is a calcium salt.

20. The method of claim 16 characterized further in that the carbonated, basic alkaline earth metal salt is a mixture of salts of a sulfonic acid and a carboxylic acid having a weight ratio of the sulfonic acid salt:carboxylic acid salt from about 1:1 to 1:4.

(References on following page)

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## References Cited by the Examiner

## UNITED STATES PATENTS

|           |         |                    |          |   |
|-----------|---------|--------------------|----------|---|
| 2,616,905 | 11/1952 | Asseff et al. .... | 252—39   | X |
| 2,616,924 | 11/1952 | Asseff et al. .... | 252—33.6 | X |
| 2,629,692 | 2/1953  | Liehe .....        | 252—33.2 |   |
| 2,695,910 | 11/1954 | Asseff et al. .... | 252—33   | X |
| 2,839,470 | 6/1958  | Warren .....       | 252—39   |   |

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## 14

|           |         |                      |          |   |
|-----------|---------|----------------------|----------|---|
| 2,854,408 | 9/1958  | Brugmann et al. --   | 252—33.2 | X |
| 2,915,467 | 12/1959 | McCormick .....      | 252—39   |   |
| 2,971,014 | 2/1961  | Mastin .....         | 252—42.7 | X |
| 3,027,325 | 3/1962  | McMillen et al. .... | 252—18   | X |

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