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COMPLEX BASIC SOAP GREASES

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This invention relates to lubricating compositions containing "complex basic soaps" and has special reference to greases containing these soaps. This application is a continuation-in-part of my copending application Serial No. 473,217 filed January 22, 1943.

The object of the invention is to obtain all the benefits in such lubricants and greases as are peculiar to complex basic soaps. Complex basic soaps produce stable greases which have excellent melting point and penetration characteristics, do not require hydration, have exceptional resistance to deterioration by the action of heat and by the action of moisture including boiling water and have unusual thickening effects on lubricating oils even at relatively low concentrations. An especially important fact is that stable greases are formed with high viscosity oils of both paraffinic and naphthenic types. Another object of this invention is to provide processes for the manufacture of complex basic soap lubricants.

By the term "complex basic soap" as used in this application it is meant to include products in which at least two metals are present and in which the ratio of equivalents of combined metals to equivalents of saponified high molecular weight organic acids is greater than 1.1:1 and preferably is greater than about 1.2:1. Depending upon the particular saponifiable material and upon the characteristics of the mineral oil employed it is preferred that this ratio be between about 1.2:1 and 2:1 but it may be as high as 3:1 or even as high as 4:1. Further, even though the ratio of equivalents of combined metals to equiva'ents of saponified high molecular weight organic acids is greater than 1:1, the complex basic soaps of this invention are substantially neutral or substantially free from readily titratable excess alkalinity at least beyond a relatively small amount.

By the term "normal soap" as used in this application it is meant to include those products which result when one equivalent of a metal hydroxide or a mixture of metal hydroxides or other basically reacting metal compounds is reacted with one equivalent of a saponifiable material to form a soap, said soap being the normal metal salt of the high molecular weight organic acid present as such or derivable by saponification from the saponifiable material.

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Examples of saponifiable materials containing high molecular weight organic acids present as such or readily derivable therefrom by saponification include fats such as tallow, lard oil, hog fat, horse fat, etc., high molecular weight organic acids such as stearic acid, oleic acid, the high molecular weight acids resulting from the oxidation of petroleum fractions (for example, paraffin wax and mineral oil), rosin and related products, high molecular weight naphthenic acids, sulfonic acids, etc., and saponifiable waxes such as beeswax, sperm oil, degras, etc.

One of the metals employed in the formation of the complex basic soaps of the present invention must be polyvalent and is preferably selected from the alkaline earth metals, barium, calcium, strontium, and magnesium. However, aluminum, beryllium, zinc, cadmium, boron, tin, zirconium, cerium, vanadium, antimony, bismuth, arsenic, copper, molybdenum, germanium, columbium, chromium, selenium, tellurium, tungsten, manganese, iron, cobalt, or nickel may be used as the polyvalent metal. The second metal must be different from the first and is preferably an alkali metal, namely, lithium, sodium, potassium, or cesium, or an alkaline earth metal, namely, barium, calcium, strontium, or magnesium although the other metals listed above may also be used. It is not meant to indicate that the complex basic soaps of this invention are limited to the use of two metals, as three or even more metals can be employed but in any event at least one of the metals must be polyvalent.

The present invention resides in lubricating compositions, especially greases, which contain complex basic soaps which are substantially neutral or substantially free from readily titratable excess alkalinity. While the invention may be extended to freely fluid lubricants, such as Diesel engine lubricating oils containing small proportions of complex basic soaps, it includes more particularly the use of such complex basic soaps in proportions to thicken lubricating oils appreciably for the purpose of producing liquid greases or solid greases of varying consistencies. More particularly, the invention resides in mineral oil lubricants containing thickening proportions of complex basic soaps where the ratio of equivalents of combined metals to equivalents of saponified high molecular weight organic acids is

between about 1.2 and 2, although it extends to the upper limit above indicated, i. e., 4 to 1, and may be as low as 1.1:1. Especially stable complex basic soap greases have been found to have a ratio within the range of 1.3 to 1 and 1.9:1. The invention also comprises the method of making such lubricants.

The invention also includes the use of complex basic soaps to produce lubricants employing high viscosity mineral oils, e. g., 50 or 70 S. A. E. grade or even bright stocks as well as lower viscosity mineral oils, e. g., 20 or 30 S. A. E. grade. For some purposes it has even been found desirable to incorporate as much as 25% or even more of asphalt in the complex basic soap greases of this invention. Good lubricants may also be produced from the very low viscosity "bottoms" fraction obtained by fractionating heavy alkylates obtained from alkylation processes in the manufacture of motor and aviation fuels from certain stocks where said bottoms have a viscosity in the order of that of spray oils or even lower.

In connection with the present complex basic soaps it has been found that under appropriate conditions it is possible to react one equivalent weight of a saponifiable material (as determined by its saponification number) with more than about 1.1 and up to about twice the equivalent weight (or even up to a ratio of 4 as above indicated) of a mixture of basically reacting metal compounds, such as for example strontium hydrate and calcium hydroxide, to produce a material which is substantially neutral or substantially free from readily titratable excess alkalinity. Although it is within the scope of the present invention to react directly one equivalent of a saponifiable material with more than one equivalent of a mixture of the basically reacting compounds of two or more metals, it is preferred to prepare the complex basic soaps by first forming a normal soap by reacting one equivalent of a saponifiable material with one equivalent of a basically reacting metal compound, for example strontium hydrate. Subsequently, the desired number of equivalents of a basically reacting compound of another metal, such as for example one equivalent of calcium hydroxide, is then added and the mixture heated until the product is substantially neutral or substantially free from readily titratable excess alkalinity. In either case, the resultant material is a complex basic soap of the present invention. The latter can be formed in the presence of oil to produce a grease or fluid lubricant directly or the complex basic soap can be formed in the absence of oil and later compounded with oil to form the desired lubricant.

Although I do not wish to be limited by the theories advanced herein, the net reaction which appears to occur and which results in the formation of the improved greases forming the subject of this invention is the oxidation of a portion of the saponifiable material and reaction of the basically reacting metal compounds with the remaining saponifiable material and the acidic products formed. It is likely that regardless of the particular procedure used, the initial reaction which occurs in the formation of a normal soap by the saponification of the saponifiable material with an equivalent quantity of a basically reacting metal compound. Subsequently a portion of the normal soap is oxidized by oxygen and the excess basically reacting metal compound present, and added either prior to or after the

formation of the normal soap, combines with the acidic materials formed.

The character of the oxidation reaction which occurs is probably influenced by the presence of the excess basically reacting metal compound or compounds and possibly by the presence of a polar solvent such as water or glycerine. In this connection evidence has been obtained indicating that in the presence of a polar solvent such as water, normal metal soaps form complexes with metal hydroxides. These complexes have a different solubility in oil than the original normal metal soap alone, but still contain the excess metal hydroxide in a readily titratable form. It is conceivable therefore that the material actually undergoing oxidation is the normal metal-soap metal hydroxide complex.

One of the principal oxidation products which results when one equivalent of a fat, saponifiable wax, or high molecular weight saponifiable organic acid is reacted with about 1.1 or more equivalents of basically reacting metal compounds under the conditions as disclosed in the present invention and illustrated in the subsequent examples, is carbon dioxide present in the final product as metal carbonate. In addition, appreciable amounts of acetic acid and relatively smaller amounts of other low molecular weight carboxylic acids, such as formic acid, propionic acid, oxalic acid, etc., also appear to be formed and are present in the final product as the corresponding metal salts. Under some conditions of oxidation coming within the scope of the present invention, metal carbonate may be the principal salt formed and may be preferred for certain combinations of mineral oil and saponifiable materials.

I have also discovered that many of the desirable properties of the complex basic soap greases formed, for example, by reacting one equivalent of calcium hydroxide with one equivalent of a saponifiable material in the presence of oil and subsequently reacting the normal calcium soap with one equivalent of strontium hydroxide to give a substantially neutral complex basic soap grease, can be obtained by mixing one mol of the normal calcium soap of the same saponifiable material with lubricating oil and subsequently adding one mol of an aqueous solution of strontium acetate and then heating to an elevated temperature to effect dehydration and dispersion in the lubricating oil. Also, greases even more closely resembling those obtained by reacting one equivalent of calcium hydroxide with one equivalent of a saponifiable material in the presence of oil and subsequently reacting the normal calcium soap with one equivalent of strontium hydroxide to give a substantially neutral complex basic soap grease have been produced by combining one mol of the normal calcium soap of the same saponifiable material with 0.5 mol of strontium acetate and 0.5 mol of strontium carbonate and dispersing the resultant product in lubricating oil.

I have also discovered that complex basic soap greases can be formed not only by the addition of a normal metal soap and the acetate salt of a different metal to a lubricating oil or a normal metal soap along with the acetate and carbonate salt of a different metal to lubricating oil, but also by compounding a normal metal soap, or a mixture of normal metal soaps lubricating oil, and a variety of salts of other different metals.

Metal salts which are useful for the foregoing purposes include preferably the simple reaction products resulting from the combination of one

equivalent of a metal oxide or metal hydroxide with one equivalent of a mineral acid or of an organic acid of relatively low molecular weight. However, I may also employ acidic or basic salts in which one equivalent of metal oxide or metal hydroxide has been reacted with more or less than one equivalent of a mineral acid or acid anhydride such as sulfuric acid, hydrochloric acid, orthophosphoric acid, pyrophosphoric acid, sulfurous acid, carbonic acid, boric acid, thiosulfuric acid, etc., SO_2, SO_3, CO_2, etc. I may also employ metal salts of organic acids of relatively low molecular weight which are relatively insoluble in lubricating oil. As examples may be cited the metal salts of monocarboxylic and polycarboxylic acids containing less than about 7 carbon atoms per molecule, such as formic, acetic, propionic, valeric, oxalic, malonic, succinic, etc., acids, the low molecular weight alkyl and aryl sufonic acids, the low molecular weight carboxylic acids, such as glyceric, glycollic, thioglycollic, etc.

In the case of greases coming within the scope of the present invention, I prefer to employ a complex of a normal metal soap with a carbonate of a metal different from that contained in the metal soap or with a monocarboxylic acid salt of a metal different from that in the metal soap, said acid having less than about 7 carbon atoms, or a mixture of any two or more of such complexes, either as such or in admixture with a normal metal soap. In the case of greases to be used under acidic conditions, such as are encountered in the canning industry, it may be desirable to employ a complex of a normal metal soap with a metal oxide or metal hydroxide in conjunction with the preferred complexes listed above. It is also within the scope of my invention to incorporate an alkaline-type filler, such as zinc oxide in the finished grease in order to overcome the effects of any acid liquors with which the greases may come in contact. In accordance with the present invention of using as lubricants complex basic soaps compounded in mineral oil, I prefer to employ more than 0.1 equivalent and preferably more than 0.2 equivalent and desirably between 0.3 and 0.9 equivalent and as high as 2.0 equivalents or even as much as 3.0 equivalents of a metal salt in conjunction with one equivalent of a normal soap of a different metal as the basic complex soap to be compounded with mineral oil to form the complex basic soap lubricants of the present invention. It follows from the above that the ratios of the different metals will be of the same magnitude, i. e., between limits of 0.1 and 3.0 equivalents of one metal to one equivalent of a different metal.

It is not meant to intimate that any given metal salt is the full equivalent of any other metal salt for modifying the characteristics of a dispersion of a normal metal soap in lubricating oil. In fact, the complexes of various metal salts with a given normal metal soap vary over a wide range as regards their respective solubilities in a given mineral lubricating oil. For example, I have found that of the various complex basic calcium soap greases coming within the scope of the present invention, those produced by reacting 0.1 or more equivalents of either strontium acetate or lithium acetate with one equivalent of normal calcium soap dispersed in mineral oil, possess unusual and highly desirable properties not exhibited by combinations of normal calcium soap with other metal salts.

It has also been noted that even though the final grease is to be substantially anhydrous, a product of improved characteristics can often be obtained by adding a small amount of water, for example, in the range of 0.1 to 3% by weight or even as high as 10% by weight of the grease charge at a suitable temperature and subsequently increasing the temperature to effect substantially complete dehydration. The grease may be at a temperature of about 210° F. or less when such water additions are made, although temperatures as high as 230° F. or even as high as 300° F. or higher may be used, and subsequent dehydration has been accomplished by heating to temperatures in the neighborhood of 250° F. or higher when necessary. With certain saponification reagents the greases produced by the processes of the present invention have a granular appearance, but by employing the hydration-dehyration technic, products of smooth buttery texture are obtained often accompanied by an increase in consistency and melting point. Further improvements in grease texture can likewise usually be obtained by working the grease at temperatures below about 200° F. and preferably below about 150° F. prior to final packaging.

Normally in reacting a saponifiable material with an excess of basically reacting metal compounds the extent of the oxidation reaction is controlled so as to produce a final grease which is substantially neutral or free from readily titratable excess alkalinity, that is, one having a free acid or free alkali content less than about the equivalent of 5.0 mg. KOH per gram of soap present. In other words, the oxidation is so controlled that it results in the formation of at least about 0.1 equivalent of acidic oxidation products and preferably about 0.2 to 1.0 equivalent of acidic oxidation products or even as high as about 3.0 equivalents of acidic oxidation products. The progress of the oxidation reaction can be followed by periodically titrating to determine the proportion of unreacted basic material present in the reacting mass, which has not combined with acidic oxidation products and when this has reached the desired value, the oxidation may be arrested such as by rapidly cooling to a temperature below about 250° F. to 300° F. While it is preferred that the complex basic soaps in lubricants of this invention be substantially neutral, they may contain a small amount of free acidity or alkalinity. The finished grease may have a free alkali content calculated as metal hydroxide as high as about 0.5% by weight of grease or a free acid content equivalent to about 2.0 mg. KOH per gram of grease. A grease having a free acid content may be obtained by either continuing the oxidation to produce an excess of acidic reaction products over that required to neutralize the free basically reacting material or the oxidation reaction can be stopped at an earlier stage, such as while free basically reacting material is still present, and fatty acid or other acidic materials added in sufficient quantity to give a grease of the desired free acid content. In order to obtain a free alkali content the oxidation can be stopped at an intermediate point or it can be continued to produce a substantially neutral or even acidic soap and the desired excess of basically reacting compound then added.

Usually the hydration-dehydration technique to produce a final substantially anhydrous grease is most effective on a slightly acidic complex basic soap grease. Subsequently the grease can be adjusted to the desired acidity or alkalinity by the addition of a metal hydroxide or acid, as the case

may be. In a similar manner complex basic soap greases prepared by compounding normal metal soap with a salt of a different metal can be rendered acidic or alkaline as desired by adding fatty acids or other acidic materials or metal hydroxide or other basically reacting metal compounds, as the case may be.

Free alkalinity is measured in accordance with A. S. T. M. method of test No. D–128–40, section 18, except that titration is conducted in the cold and the titration is made directly with standard HCl solution rather than by adding an excess of HCl solution and then back titrating with alcoholic potassium hydroxide solution. Free acidity is measured in accordance with A. S. T. M. method of test No. D–128–40, section 20. Briefly, the methods of test employed are as follows:

A 10 gram sample of the grease is weighed to the nearest tenth of a gram into a 250 ml. Erlenmeyer flask. To the flask is then added 75 ml. of petroleum ether and 50 ml. of 95% alcohol containing phenolphthalein indicator, the alcohol having been previously made neutral as indicated by the phenolphthalein indicator. The flask is stoppered and shaken vigorously in the cold until the grease has completely disintegrated and no lumps remain. The solution is then allowed to settle and free alkali or free acid, as observed by the color of the alcoholic layer, is titrated carefully in the cold to the phenolphthalein end point with 0.5 normal HCl or alcoholic KOH, as required. Free alkalinity is calculated in terms of metal hydroxide; free acidity in terms of oleic acid or acetic acid. Free alkalinity and free acidity may also be expressed in terms of equivalent mg. of KOH per gram of grease or soap as desired.

Since the formation of complex basic soaps from a fat, saponifiable wax or high molecular weight saponifiable organic acid and an excess of basically reacting metal compounds in part involves an oxidation reaction, it is necessary that this reaction be conducted in the presence of air or other oxygen-containing gas. Further, preferably, the reaction should be conducted in the presence of a polar solvent such as, for example, water or glycerine. If desired, a portion or all of the mineral oil can be blended with the saponifiable material and reaction with the basically reacting metal compounds subsequently conducted. Under these conditions the mineral oil appears to serve essentially only as an inert diluent. On the other hand, the saponifiable material can be reacted with the basically reacting metal compounds in the absence of mineral oil thereby forming a concentrate which can be subsequently compounded with mineral oil to form a grease. When a complex basic soap or complex basic soap grease is to be formed by reacting a normal metal soap with a metal salt or a mixture of metal salts, similar procedures can be followed except that the presence of oxygen-containing gas is not necessary and may even be undesirable; on the other hand, it does appear preferable at some stage in the compounding procedure to have a polar solvent present in order to effect formation of the complex from the normal metal soap and metal salt.

As indicated hereinabove, in order for the desired oxidation reaction and normal metal soap metal salt complex formation to proceed within the preferred temperature range it is usually desirable that at least a small percentage of a polar solvent, in the neighborhood of at least about 0.1% by weight of the reacting mass, be present. Further, it appears that preferably this polar solvent should be water, although under some conditions the oxidation and complex formation proceeds more readily in the presence of a mixture of water and glycerine, water and glycol, or with some hydroxy or polyhydroxy organic compound, such as ethyl alcohol, diethylene glycol, etc. Preferably the proportion of polar solvent present should be in the range of 0.5% to 4.0% by weight of the reacting mass, but under some conditions smaller quantities, such as about 0.1% and higher quantities, such as about 10% can be used. As an indication of the desirability of having at least a small percentage of a polar solvent present, I have observed in the case of certain anhydrous normal metal soaps that when mixed with anhydrous metal hydroxides and heated in the presence of oxygen at a temperature of 350° F. to 500° F. for three hours and the mixture subsequently analysed, little or no reaction had occurred and substantially all of the metal hydroxide could be recovered unchanged. Further, if the same mixtures containing an added 0.5% of water were heated in a closed kettle under the same conditions but with oxygen excluded, little or no reaction was observed to take place. However, when the same mixtures containing 0.5% of added water were heated for three hours in contact with air or oxygen and at a temperature of 350° F. to 500° F., the resulting products contained normal metal soap along with metal carbonate and the metal salts of organic acidic oxidation products, and a corresponding amount of the metal hydroxide had disappeared.

One of the preferred methods of forming complex basic soap lubricants from a normal metal soap, a metal salt, and mineral oil is to dissolve the normal metal soap in all or only a portion of the mineral oil to be used and subsequently add a solution or a dispersion of the desired metal salt in a polar solvent, intimately mix and then while continuing the mixing boil off or evaporate all or a portion of the polar solvent. Additional oil can be added during or after the removal of the polar solvent, if desired. The normal metal soap can be preformed or it can be made in the presence or absence of the mineral oil by reacting a saponifiable material with a basically reacting metal compound, such as a metal oxide, or metal hydroxide by methods known to those skilled in the art.

Another preferred method of forming a complex basic soap lubricant from a normal metal soap, a metal salt, and mineral oil is to dissolve the desired normal metal soap in mineral oil or form the normal metal soap from the desired saponifiable material and a basically reacting metal compound such as a metal oxide or metal hydroxide in the presence of all or a part of the desired mineral oil. Subsequently, a complex is formed between the normal metal soap and a metal oxide or metal hydroxide, added in an amount equivalent to the amount of salt which it is desired to complex with the normal metal soap, in the manner described in the preceding paragraph, except that the polar solvent need not be removed. Finally the acid of the desired salt in an amount equivalent to the added metal oxide or metal hydroxide is introduced and all or a part of the polar solvent, then removed by heating to a temperature within the range of about 200° F. to 600° F. Additional mineral oil can be added at any or all stages of the compounding as will be obvious to one skilled in the art.

As a special case of the preferred method described in the preceding paragraph, the desired saponifiable material can be reacted with an amount of a mixture of basically reacting metal compounds such as for example, strontium hydroxide and calcium hydroxide equal to that required to react with the saponifiable material and with the acid whose metal salt is desired in the complex. After the saponification has been completed the acid of the desired metal salt can be added in quantity just sufficient to neutralize the excess metal oxide or metal hydroxide present. It is also possible under this special case to mix the desired saponifiable material with the acid whose metal salt is desired in the complex and then add an amount of a mixture of metal oxides or metal hydroxides or other basically reacting metal compounds sufficient to finally effect the saponification, form the salt and produce the complex. If it is desired to produce a final product having a free alkali or free acid content the desired acidity or alkalinity can be introduced at any of several stages as will be obvious to one skilled in the art.

It is of particular interest to note that the greases constituting the subject of this invention can usually be produced as substantially anhydrous products having a stable grease structure. However, under some conditions and in order to obtain certain specific characteristics it may be desirable to produce greases containing small amounts of water, for example less than about 1.0% and preferably less than about 0.5%. It will be obvious to one skilled in the art that this amount of water can be incorporated at any of several stages in the process of making the grease. For example, if the grease has less than the desired amount of water, the required additional water can be added and worked into the grease at a temperature of 200° F. or less prior to drawing. On the other hand, if desired, an excess of water can be added to the grease before or after all of the oil has been incorporated or even during addition of oil and when the temperature is in the neighborhood of 210° F. or less or even at more elevated temperatures such as 220° F. to 300° F. and the excess water subsequently removed by increasing the temperature of the grease if necessary and then cooling after the desired water content has been reached.

The formation of the complex basic soap greases of this invention generally requires high temperatures, preferably in the region of about 400° F. to 550° F., although they can be formed over a wider temperature range such as about 250° F. to 600° F. In forming normal metal soaps and complex basic soaps by reacting a saponifiable material with basically reacting metal compounds, the bases are added preferably as metal hydroxides although in some instances metal oxides, metal carbonates, etc., may be employed. The bases may be added as a powder, small granules, or as an aqueous or oil slurry, as desired. Either normal or complex basic soap formation is preferably carried out in the presence of part of the lubricating oil to be used in the finished grease, although inert low-boiling solvents may be used under pressure and subsequently evaporated to leave a pure soap residue. The powder can then be dispersed in a mineral oil and a complex basic soap lubricant formed.

The amount of complex basic soap to be incorporated in the greases of this invention may be from about 5% to about 50%, although concentration as low as about 2% and as high as about 75% may be desirable for certain special combinations and applications.

Complex basic soaps may also be used in relatively small proportions to produce liquid greases and fluid lubricants, such as lubricating oils for internal combustion engines, especially Diesel engines. The soap concentrations in such applications are usually below about 5% and are normally in the range of 0.2% to about 2.0%. However, by a proper choice of saponifiable material, metal salt, and mineral oil, it is possible to produce a fluid lubricant containing as high as 10% by weight of complex basic soap or even higher.

Materials other than complex basic soaps may also be added to the lubricating compositions of this invention, such as water, alcohols, and other solvents, anti-oxidants, fillers, etc., as desired. An especially hard grease, for example, was prepared by the incorporation of an oil containing about 40% of asphalt instead of the usual lubricating oil. Additions of petrolatum and solvent extracts from lubricating oil stocks have been helpful in some instances.

In addition to using both light and heavy mineral lubricating oils to make complex basic soap lubricants, I may also employ the light lubricating-type oil which is recovered as heavy bottoms from the distillation of residuals obtained in modern alkylation processes employed in making alkylated motor fuels from some stocks. In some such processes the mentioned residuals are recovered in fairly large proportions. About 80% thereof is then distilled off to be used for various purposes, thereby leaving about 20% of the heavy alkylated bottoms mentioned. This 20% fraction may be further cut to yield lighter and heavier fractions. These fractions have viscosities in the order of that of spray oil and of very light lubricating oil, e. g., S. A. E. 10. In view of the properties of the complex basic soaps hereof, such heavy alkylated bottoms may be used as the lubricating fraction, especially where a light oil is desirable for a given fluid or grease-like product having a low pour point. The described bottoms may, for example, be recovered from the sulfuric acid alkylation process described in the "Refiner" for September, 1941, vol. 20, page 378. Suitable bottoms are obtained, for example, after recovery of the motor fuel alkylate. Some stocks yield larger amounts of such alkylate bottoms than others. These bottoms may in turn be fractionated for the present purpose.

The following examples will serve as illustrations of the present invention:

Example I

To 772 g. of tallow (saponification number=198; equivalents=2.72) and 118 g. of sperm oil (saponification number=133; equivalents=0.28) dissolved in 1500 g. of a naphthenic-type SAE 20 lubricating oil was added 213 g. of an aqueous solution of caustic soda (NaOH content=47%; equivalents=2.51) and the mixture was heated until saponification was substantially complete. Then 450 grams of barium hydrate ($Ba(OH)_2$ content=53%; equivalents=2.79) and 620 g. of the same lubricating oil were added slowly and the mixture heated with agitation until substantially all the water had been evaporated and the free alkalinity of the mixture calculated as $Ba(OH)_2$ amounted to 0.3%. Since the total weight of the product at this point was about 3276 g., 0.3% of free alkalinity amounted to

about 10 g. of $Ba(OH)_2$ or 0.12 equivalents, whereas the excess of basic equivalents

(2.51+2.79=5.30)

over acid equivalents (2.72+0.28=3.00) in the charge was 2.30, or nearly 20 times as great.

The above complex basic soap concentrate was diluted with about 3580 g. of a naphthenic-type S. A. E. 30 lubricating oil to give a substantially anhydrous grease containing about 17% by weight of soap. This product had a melting point of about 250° F., and A. S. T. M. worked penetration at 77° F. of about 345, contained about 0.1% of free alkalinity, calculated as $Ba(OH)_2$, and exhibited good water resistance.

The ratio of equivalents of combined metals (sodium+barium) to equivalents of saponified high molecular weight organic acids in the complex basic soap was determined by analysis to be about 1.85. This ratio is slightly higher than that calculated on the basis of the ingredients charged (5.30/3.00=1.77) due to the oxidation of a small amount of the saponifiable material. These data indicate that since the amount of oxidation of saponifiable material is relatively small, the ratio of equivalents of combined metals to equivalents of saponified high molecular weight organic acids in the product can be approximated from the amounts of ingredients used to form the complex basic soap.

A grease of similar characteristics was produced by reacting 2.72 equivalents of tallow and 0.28 equivalent of sperm oil with 2.51 equivalents of NaOH in the presence of oil as described above, subsequently adding 2.79 equivalents of barium hydrate and 2.29 equivalents of acetic acid, and finally dehydrating and grading with oil to give a final product of about 17% by weight complex basic soap content.

Example II

Approximately 860 g. of aluminum stearate (2.94 equivalents of aluminum and 2.00 equivalents of stearic acid) and 2000 g. of a naphthenic-type S. A. E. 30 lubricating oil were mixed and heated to 300° F. Subsequently 474 g. of barium hydrate ($Ba(OH)_2$ content=54%; equivalents=2.99) was added slowly with stirring and heating continued. The excess alkalinity gradually disappeared and a neutral product was obtained in about 6 hours. The temperature was then decreased to about 200° F. and 0.05% of water added to improve the body and smoothness of the grease. This product contained about 35% of soap and had a ratio of equivalents of combined metals to equivalents of saponified high molecular weight acids of about 3.0.

Example III

Approximately 850 g. of tallow (saponification number=193; equivalents=2.92) and 144.2 g. of an aqueous lithium hydroxide solution (LiOH content=54.85%; equivalents=3.30) and 1500 g. of a naphthenic-type S. A. E. 20 lubricating oil were mixed and heated until saponification and dehydration were substantially complete. Subsequently 438 g. of barium hydrate ($Ba(OH)_2$ content=53.6%; equivalents=2.74) was added to the above mixture and the temperature maintained at about 350° F. until the per cent of free base calculated as $Ba(OH)_2$ was reduced to 0.13%. Then 387 g. of S. A. E. 20 naphthentic type lubricating oil and 3213 g. of S. A E. 30 naphthenic-type lubricating oil were incorporated in the above concentrate to obtain a grease containing only

0.04% of free alkalinity calculated as $Ba(OH)_2$. The ratio of equivalents of combined metals to equivalents of saponified high molecular weight organic acids was about 2.1 and the soap content was approximately 23% by weight. The resultant substantially anhydrous grease had a Ubbelohde melting point of 285° F. and an A. S. T. M. worked penetration at 77° F. of 290.

A grease of similar properties was obtained by following the same procedure as outlined above except that 3.0 equivalents of propionic acid was added along with the barium hydrate followed by heating to 350° F. for only sufficient time to effect substantially complete dehydration.

Example IV

Approximately 0.293 gram-equivalents of the same tallow as used in Example III was mixed with 0.250 gram-equivalents of sodium hydroxide, added as a 46.8% aqueous solution and 200 grams of S. A. E. 20 naphthenic-type lubricating oil. This mixture was heated until saponification and dehydration had taken place. Then 0.293 gram-equivalents of magnesium hydroxide was added and heating continued at a temperature of approximately 500° F. until all the excess alkalinity had disappeared. Finally, 30 grams of S. A. E. 30 and 280 grams of S. A. E. 20 naphthenic-type lubricating oils were added as the mixture cooled. The resulting product contained a small amount of free acidity equivalent to a neutralization number of 4.0 mg. of KOH per gram of sample. The grease contained about 15% of soap and had a ratio of equivalents of combined metals to equivalents of saponified high molecular weight organic acids of about 2.1. The grease had a Ubbelohde melting point of 390° F., and A. S. T. M. penetration of 435, a dark green color, a very smooth texture and was very stable.

Example V

Approximately 50 grams of a conventional cup grease, containing 9 grams of calcium tallow soap (0.03 equivalents), was mixed with 3.5 grams of strontium acetate (0.034 equivalents) dissolved in water and while agitating the mixture was heated to a temperature of 350° F. to effect substantially complete dehydration and form the complex basic soap. Subsequently the material was cooled to room temperature and worked to give a transparent grease of smooth texture. This product, which was extremely resistant to decomposition by water, had an A. S. T. M. penetration at 77° F. of 300, an A. S. T. M. dropping point in excess of 450° F., and was substantially neutral.

A grease of similar properties was prepared by mixing 50 grams of the same cup grease with 4.5 grams of strontium hydroxide octahydrate (0.034 equivalents), subsequently heating to a temperature of 450° F., maintaining at this temperature until the material was substantially neutral and finally cooling to room temperature and working.

The foregoing description of my invention is not to be taken as limiting my invention but only as illustrative thereof since many variations may be made by those skilled in the art without departing from the scope of the following claims.

I claim:

1. A lubricating composition comprising mineral oil and a metal soap complex, said soap complex having atoms of at least two different metals, at least one of which is polyvalent, and containing a ratio of equivalents of metals to equivalents of saponified high molecular weight or-

ganic acids between about 1.1 and 4 and being substantially free from readily titratable excess alkalinity, in which the ratio of equivalents of the different metals is between 0.1 and 3.0.

2. A lubricating composition comprising mineral oil and a metal soap complex, said soap complex having atoms of at least two different metals, at least one of which is polyvalent, and containing a ratio of equivalents of metals to equivalents of saponified high molecular weight organic acids between about 1.1 and 4 and being substantially free from readily titratable excess alkalinity, said composition being substantially anhydrous, in which the ratio of equivalents of the different metals is between 0.1 and 3.0.

3. A lubricating composition according to claim 1, in which the ratio of equivalents of metals to equivalents of saponified high molecular weight organic acids is between about 1.3 and 1.9.

4. A lubricating composition according to claim 1, in which the soap complex comprises a normal metal soap and a metal salt of a mineral acid in which the ratio of equivalents of metal salt to equivalents of normal metal soap is greater than about 0.1.

5. A lubricating composition according to claim 1, in which the soap complex comprises a normal metal soap and a metal salt of a low molecular weight organic acid and in which the ratio of equivalents of metal salt to equivalents of normal metal soap is greater than about 0.1.

6. A lubricating composition according to claim 1, in which the soap complex comprises a normal metal soap and a metal salt of a mineral acid in which the ratio of equivalents of metal salt to equivalents of normal metal soap is between about 0.2 and 2.0.

7. A lubricating composition according to claim 1, in which the soap complex comprises a normal metal soap and a metal salt of a low molecular weight organic acid and in which the ratio of equivalents of metal salt to equivalents of normal metal soap is between about 0.2 and 2.0.

8. A lubricating composition according to claim 1, in which the soap complex is made by reacting in excess of one equivalent of a basically reacting metal compound with one equivalent of a saponifiable material.

9. A lubricating composition according to claim 1, in which the soap complex is made by reacting normal metal soap and a metal salt of mineral acid.

10. A lubricating composition according to claim 1, in which the soap complex is made by reacting normal metal soap and a metal salt of a low molecular weight organic acid.

11. A lubricating composition according to claim 1, in which the soap complex is made by reacting normal metal soap, basically reacting metal compound and a mineral acid, the amount of mineral acid being sufficient to neutralize said basically reacting metal compound.

12. A lubricating composition according to claim 1, in which the soap complex is made by reacting normal metal soap, basically reacting metal compound and a low molecular weight organic acid, the amount of said acid being sufficient to neutralize said basically reacting metal compound.

13. A lubricating composition according to claim 1, in which one of the metals is an alkaline earth metal and the remaining metals are from the class consisting of alkaline earth metals and alkali metals.

14. A lubricating composition according to claim 1, in which one of the metals is an alkaline earth metal and one of the metals is an alkali metal.

15. A lubricating composition according to claim 1, wherein said two different metals are barium and aluminum.

16. A lubricating composition according to claim 1, wherein said two different metals are barium and sodium.

17. A lubricating composition according to claim 1, wherein said two different metals are magnesium and sodium.

18. A lubricating composition comprising mineral oil and a minor proportion of a metal soap complex containing at least two different metals, at least one of which is polyvalent, said soap complex being produced by reacting substantially equal equivalents of basically reacting metal compounds and saponifiable high molecular weight organic acids to substantially complete saponification and then reacting the soap product with an appreciable additional quantity of a basically reacting compound of another metal in the presence of oxygen at temperatures between approximately 300° F. and 600° F. until the product is substantially free from readily titratable excess alkalinity, said soap complex having a ratio of equivalents of metals to saponifiable high molecular weight organic acids in excess of about 1.1, in which the ratio of equivalents of the different metals is between 0.1 and 3.0.

19. A lubricating composition comprising mineral oil and a metal soap complex prepared by reacting at least 1.2 equivalents of basically reacting compounds of at least two different metals, at least one of which is polyvalent, with one equivalent of saponifiable high molecular weight organic acids at temperatures between about 400° F. and 550° F. in the presence of oxygen until the product is substantially free from readily titratable excess alkalinity, in which the ratio of equivalents of the different metals is between 0.1 and 3.0.

20. A lubricating composition as in claim 19, in which the soap complex is prepared by reacting said basically reacting metal compounds and said high molecular weight organic acid in the presence of mineral oil.

21. A lubricating composition comprising mineral oil and a soap complex containing at least 1.2 equivalents of metals to one equivalent of saponified high molecular weight organic acids, said soap complex being prepared by reacting an aluminum soap with an appreciable portion of a basically reacting compound of an alkaline earth metal at temperatures between about 300° F. and 600° F. in the presence of oxygen until the soap product is substantially free from readily titratable excess alkalinity, in which the ratio of equivalents of the different metals is between 0.1 and 3.0.

22. A lubricating composition according to claim 21, in which said aluminum soap is aluminum stearate and said alkaline earth metal is barium.

23. A method of preparing lubricants comprising reacting a saponifiable material with an approximately equal chemical equivalent of a basically reacting metal compound in the presence of mineral oil under saponifying conditions until saponification is complete and then reacting the soap product with an additional quantity of a basically reacting compound of a different metal at temperatures between about 400° F. and 550° F. in the presence of oxygen to yield a soap com-

plex which is substantially free from readily titratable excess alkalinity, which contains at least two different metals, at least one of which is polyvalent and which contains a ratio of equivalents of metals to equivalents of saponified material of at least 1.1, cooling the final reaction mixture and adding additional mineral oil, in which the ratio of equivalents of the different metals is between 0.1 and 3.0.

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