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LUBRICANTS

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This invention relates to lubricating compositions containing basic strontium soaps and has special reference to basic strontium soap greases. This application is a continuation-in-part of my copending application, Serial No. 469,894, filed December 23, 1942.

The object of the invention is to obtain all the benefits in such lubricants and greases as are peculiar to basic strontium soaps. Basic strontium 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 in contrast to the inability of some basic soaps to effect proper thickening of both types of such oils. Another object of this invention is to provide processes for the manufacture of basic strontium soap lubricants.

By the term "basic strontium soap" as used in this application, it is meant to include products which are substantially neutral or substantially free from readily titratable excess alkalinity, at least beyond a relatively small amount, and in which the ratio of equivalents of combined strontium to equivalents of saponified higher molecular weight organic acids is greater than 1.1 to 1 and preferably is greater than about 1.2 to 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 to 1 and 2 to 1 but it may be as high as 3 to 1 or even as high as 4 to 1.

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

Examples of saponifiable materials containing higher 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., higher molecular weight organic acids such as stearic acid, oleic acid, the higher molecular weight acids resulting from the oxidation of petroleum fractions (for example,

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paraffin wax and mineral oil), rosin and related products, higher molecular weight naphthenic acids, sulfonic acids, etc., and saponifiable waxes such as beeswax, sperm oil, degreas, etc.

The present invention resides in lubricating compositions, especially greases, which contain basic strontium 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 basic strontium soaps, it includes more particularly the use of such basic strontium 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 basic strontium soaps where the ratio of equivalents of combined strontium to equivalents of saponified higher 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 to 1. Especially stable basic strontium soap greases have been found to have a ratio within the range of 1.3 to 1 and 1.9 to 1. The invention also comprises the method of making such lubricants.

The invention also includes the use of basic strontium 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. 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 basic strontium 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 basically reacting strontium compound, such as strontium hydrate, to produce a material which is substantially neutral or free from readily titratable excess alkalinity.

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 por-

tion of the saponifiable material and reaction of the excess saponification reagent with the acidic products formed. It is likely that the initial reaction which occurs is the formation of a normal strontium soap by the saponification of the saponifiable material with an equivalent amount of the basically reacting strontium compound. Subsequently, a portion of the soap is oxidized by oxygen and the excess basically reacting strontium compound present combines with the acidic materials formed. The character of the oxidation reaction which occurs is undoubtedly influenced by the presence of the excess basically reacting strontium compound 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 strontium soap forms a complex with strontium hydroxide. This complex has a different solubility in oil than normal strontium soap alone but still contains the strontium hydroxide in a readily titratable form. It is probable, therefore, that the material actually undergoing oxidation is the normal strontium soap-strontium hydroxide complex.

One of the principal oxidation products which results when one equivalent of a fat, saponifiable wax, or a higher molecular weight saponifiable organic acid is reacted with about 1.1 or more equivalents of a basically reacting strontium compound under the conditions as disclosed in the present invention and illustrated in the subsequent examples, is acetic acid present in the final product as strontium acetate. In addition, appreciable amounts of carbon dioxide 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 strontium salts. Under some conditions of oxidation coming within the scope of the present invention, strontium 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 basic strontium soap greases having many of the desirable properties of basic strontium soap greases formed by reacting, for example, 2.0 equivalents of a basically reacting strontium compound with one equivalent of a fat, saponifiable wax, or a higher molecular weight saponifiable organic acid, can be obtained by mixing one mol of the normal strontium soap of the same fat, saponifiable wax, or higher molecular weight saponifiable organic acid with lubricating oil, 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 about 2.0 equivalents of a basically reacting strontium compound with one equivalent of a fat, saponifiable wax, or higher molecular weight saponifiable organic acid, have been obtained by combining one mol of the normal strontium soap of the same fat, saponifiable wax, or higher molecular weight saponifiable organic acid 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 basic strontium soap greases can be formed, not only by the addition of normal strontium soap and strontium acetate to a lubricating oil or normal strontium soap, strontium acetate, and strontium carbonate to

lubricating oil, but also by compounding normal strontium soap, lubricating oil, and a variety of other strontium salts.

Strontium salts which are useful for the foregoing purpose include preferably the simple reaction products resulting from the combination of one equivalent of a strontium oxide or strontium 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 strontium oxide or strontium 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 strontium salts of organic acids of relatively low molecular weight which are relatively insoluble in lubricating oil. As examples may be cited the strontium 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 sulfonic acids, the low molecular weight substituted carboxylic acids, such as glyceric, glycollic, thio-glycollic, etc., acids, the low molecular weight phenolic and thiophenolic compounds such as phenol, cresol, thiophenol, etc.

In the case of greases coming within the scope of the present invention, I prefer to employ a complex of a normal strontium soap with a metal carbonate or with a metal salt of a monocarboxylic 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 normal strontium 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 strontium soap with a strontium oxide, or strontium 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 basic strontium 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 strontium salt in conjunction with one equivalent of a normal strontium soap as the basic strontium soap to be compounded with mineral oil to form the basic strontium soap lubricants of the present invention.

It is not meant to intimate that any given strontium salt is the full equivalent of any other strontium salt for modifying the characteristics of a dispersion of normal strontium soap in lubricating oil. In fact, the complexes of various strontium salts with a given normal strontium soap vary over a wide range as regards their respective solubilities in a given mineral lubricating oil. For example, a normal strontium stearate-strontium carbonate complex is more soluble in a given mineral oil than is a normal strontium stearate-strontium formate complex. Likewise, the latter complex appears to be more soluble than one formed from normal strontium stearate and strontium acetate. Complexes of a

given normal strontium soap with certain strontium salts will possess just the proper characteristics to form with a specific mineral oil a grease of the improved properties described herein. Other complexes of the same normal strontium soap with different strontium salts will be either too soluble or insufficiently soluble to form desirable greases in the given mineral oil. In the latter case it is possible and desirable to form excellent greases coming within the scope of the present invention by mixing a complex which is too soluble in the specific mineral oil with one possessing inadequate solubility. The exact proportions of the two complexes will depend upon the relative solubilities of the two complexes and can be readily determined by one skilled in the grease-making art.

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 3.0% 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-dehydration 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 a basically reacting strontium compound 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 strontium hydroxide present in the reacting mass, which was 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 soaps in greases 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 strontium 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 strontium hydroxide or the oxidation reaction can be stopped at an earlier stage, such as while free strontium hydroxide 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 free strontium hydroxide then added.

Usually the hydration-dehydration technique to produce a final substantially anhydrous grease is most effective on a slightly acidic basic strontium soap grease. Subsequently the grease can be adjusted to the desired acidity or alkalinity by the addition of strontium hydroxide or acid, as the case may be. In a similar manner basic soap greases prepared by compounding normal strontium soaps with strontium salts can be rendered acidic or alkaline as desired by adding fatty acids or other acidic materials or strontium hydroxide or other basically reacting strontium compounds, as the case may be.

Free alkalinity is measured in accordance with 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, which has 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 strontium 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 basic strontium soaps from a fat, saponifiable wax or higher molecular weight saponifiable organic acid and an excess of a basically reacting strontium compound 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 strontium compound 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 strontium compound in the absence of mineral oil thereby forming a concen-

trate which can be subsequently compounded with mineral oil to form a grease. When a basic strontium soap or basic strontium soap grease is to be formed by reacting a normal strontium soap with a strontium salt or a mixture of strontium 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 molecular complex from the normal strontium soap and strontium salt.

As indicated hereinabove, in order for the desired oxidation reaction and normal strontium soap-strontium 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 strontium soaps that when mixed with anhydrous strontium hydroxide and heated in the presence of oxygen at a temperature of 350° F. to 500° F. for three hours and the mixture subsequently analysed, it was found that little or no reaction had occurred and substantially all of the strontium 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 mixture containing 0.5% of added water was heated for three hours in contact with air or oxygen and at a temperature of 350° F. to 500° F., the resulting product contained normal strontium soap along with strontium carbonate and the strontium salts of organic acidic oxidation products, and a corresponding amount of the strontium hydroxide had disappeared.

One of the preferred methods of forming basic strontium soap lubricants from a normal strontium soap, a strontium salt, and mineral oil is to dissolve the normal strontium 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 strontium 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 strontium soap can be performed or it can be made in the presence or absence of the mineral oil by reacting a saponifiable material with a basically reacting strontium compound, such as strontium oxide, or strontium hydroxide by methods known to those skilled in the art.

Another preferred method of forming a basic strontium soap lubricant from a normal strontium

soap, a strontium salt, and mineral oil is to dissolve the desired normal strontium soap in mineral oil or form the normal strontium soap from the desired saponifiable material and a basically reacting strontium compound such as strontium oxide or strontium hydroxide in the presence of all or a part of the desired mineral oil. Subsequently, a complex is formed between the normal strontium soap and strontium oxide or strontium hydroxide, added in an amount equivalent to the amount of salt which it is desired to complex with the normal strontium 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 strontium oxide or strontium 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 basically reacting strontium compound such as strontium oxide or strontium hydroxide equal to that required to react with the saponifiable material and with the acid whose strontium 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 strontium oxide or strontium hydroxide present. It is also possible under this special case to mix the desired saponifiable material with the acid whose strontium salt is desired in the complex and then add an amount of strontium oxide or strontium hydroxide or other basically reacting strontium compound 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 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 300° F. to 600° F. In forming normal strontium soaps and basic strontium soaps by reacting a saponifiable material with a basically reacting strontium compound, the base is added preferably as the hydroxide ($\text{Sr}(\text{OH})_2$) or as strontium hydrate ($\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$), although in some instances strontium oxide, strontium carbonate, etc., may be employed. The base may be added as a powder, small granules, or as an aqueous or oil slurry, as desired. Either normal or basic strontium 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. Particularly in the case of normal strontium soaps it is entirely possible to prepare dry soap powder by reacting, for example, oleic acid with an aqueous solution of strontium hydroxide and subsequently dehydrating. The powder can then be dispersed in a mineral oil and a basic soap formed by reacting with a strontium salt or with excess strontium hydroxide. It is also possible to prepare a basic soap powder which can subsequently be dispersed in mineral oil to form a basic soap lubricant.

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

Basic strontium 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, as indicated in one of the subsequent examples by a proper choice of saponifiable material, strontium salt, and mineral oil, it is possible to produce a fluid lubricant containing as high as 10% by weight of basic strontium soap or even higher.

Materials other than basic strontium soaps may also be added to the lubricating compositions of this invention, such as water, alcohols and other solvents, antioxidants, 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 to yield a grease composition similar to that of the subsequent example below. 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 basic strontium 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 proportion. 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., SAE 10. In view of the prop-

erties of the basic strontium 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

As a specific example of a basic strontium soap grease of this invention, 109 grams of cottonseed oil (approximately 0.38 equivalent), 16 grams of sperm oil (0.04 equivalent), about 60 grams of a naphthenic SAE 60 grade mineral lubricating oil and 102 grams of strontium hydrate, equal to 46.4 grams of $\text{Sr}(\text{OH})_2$ (0.76 equivalent), were heated at 200° F. to 300° F. until the vigor of the reaction subsided. Then an additional 250 grams of the same oil was added, and the mixture was heated for about 12 hours at about 500° F. at which time no substantial amount of free alkalinity remained. Finally about 466 grams of the same oil was stirred in, and the mass was cooled to room temperature. The product contained about 17% of soap, the ratio of base to acid of which, as indicated above, was about 0.76 to 0.42 or about 1.81 to 1. Its free alkali content was only 0.01, calculated as $\text{Sr}(\text{OH})_2$, or about 0.06% of the soap content, whereas if only the normal soap had been formed the free alkali content would have been about 2.2%, or about 13% of the soap content. The grease was smooth and unctuous, dark in color, and stable toward syneresis: When worked, its penetration at 77° F. by the A. S. T. M. method was 229, yet its melting point was over 400° F. by both the Ubbelohde and the A. S. T. M. dropping point methods.

Chemical analysis of the resulting product indicated it to contain 17.1% of basic soap which was composed as follows:

	Per cent by weight
Normal strontium soap	13.9
Strontium carbonate	2.2
Strontium salts of lower molecular weight organic acids	1.0

The ratio of equivalents of combined strontium to equivalents of saponified higher molecular weight organic acids in the basic strontium soap is about 1.93. This ratio is slightly higher than that calculated on the basis of the ingredients charged (1.81 as indicated above) due to the oxidation of a small amount of the saponifiable material. This data indicates that since the amount of oxidation of saponifiable material is relatively small, the ratio of equivalents of combined strontium to equivalents of saponified higher molecular weight organic acids in the product can be approximated from the amounts of ingredients used to form the product.

Example II

Approximately 145 grams of edible tallow (0.51 equivalent), 23 grams of sperm oil (0.06 equivalent), about 100 grams of a paraffinic SAE 50 grade mineral lubricating oil, and 139 grams of strontium hydrate, equal to 63.2 grams $\text{Sr}(\text{OH})_2$ (1.04 equivalents), were heated to about 300° F.,

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an additional 300 grams of the same lubricating oil was added, and the mixture was heated and stirred at about 500° F. for about 8 hours before adding the remaining 660 grams of the same lubricating oil, cooling and working. This product also contained about 17% of soap; the base to acid of which was, as indicated above 1.04 to 0.57 or about 1.8 to 1. However, it contained no free water and no free alkali. Its neutralization number was actually on the acid side and was equivalent to 0.17 mg. KOH per gram. Its texture was soft and unctuous, its color was dark and its stability toward syneresis was excellent. Its worked penetration was 313 and its melting point was unusually high, 410° F. by the Ubbelohde method, and 450° F. by the A. S. T. M. dropping point method.

Example III

A fluid lubricant was prepared in the following manner:

To 18.5 grams of dry powdered normal strontium oleate, 5 ml. of water was added dropwise and agitated to wet the soap thoroughly. Approximately 200 grams of a naphthenic type mineral oil having a viscosity of 100° F. of 207 Saybolt Universal seconds was then added and the mixture heated to 400° F. Subsequent cooling to 250° F. resulted in partial gelation. A solution of 7.6 grams of strontium hydroxide octahydrate (1.0 equivalent of strontium hydroxide per equivalent of normal strontium soap mixed in the oil) in 30 ml. of water at 200° F. was added to the soap-oil mixture at 240° F. with rapid stirring. The mixture was then heated to 400° F. with continued agitation and blowing with illuminating gas (to avoid any oxidation of either soap or mineral oil). A small portion of the material was cooled to room temperature and was observed to form a semi-translucent gel. The remaining material was blown with carbon dioxide at temperatures of 250° F. to 300° F. for one hour and then cooled to room temperature. A trace of solid material, probably uncombined strontium carbonate, settled leaving a transparent stable fluid oil. The separated clear product was diluted with additional mineral oil similar to that employed earlier in the experiment, to yield a product calculated to have a strontium oleate content of 5.0% by weight, and a strontium carbonate content of 2.0%. The diluted material had a viscosity of 246 Saybolt Universal seconds at 100° F.

A sample of this oil was tested in a Caterpillar Diesel engine in comparison with a straight mineral oil and was found to have superior detergency properties. The piston removed from the Diesel engine operated with the compounded oil showed no tendency for sticking of rings and little or no carbon or varnish deposition, whereas the piston removed from the engine operated on the straight mineral oil had stuck rings and considerable deposits of varnish and carbon.

Example IV

A basic strontium soap grease was prepared from the following ingredients:

	Grams
Tallow fatty acids.....	50.0
Acetic acid.....	10.7
Strontium hydrate.....	48.0
SAE 40 grade solvent extracted 90 V. I. oil....	200

The tallow fatty acids were charged to a large beaker, melted, subsequently mixed with 50 grams of oil and heated. When the temperature of the

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mixture was 180° F. the acetic acid was added and followed by strontium hydrate. While stirring, the temperature of the material was gradually increased to effect reaction and partial dehydration and the remaining oil gradually added. The mixture was finally heated to a temperature of 450° F. and then set aside to cool to room temperature. The cooled material was worked to a smooth unctuous grease. This substantially anhydrous, neutral product, calculated to have a normal strontium soap content of 21.0% by weight and a strontium acetate content of 6.7% by weight, was determined to have a melting point in excess of 400° F. and a consistency as measured by a modified A. S. T. M. penetration at 77° F. of 328.

For comparison, a normal strontium soap lubricant was prepared from the following ingredients:

	Grams
Tallow fatty acids.....	50.0
Strontium hydrate.....	25.3
SAE 40 grade solvent extracted 90 V. I. oil....	200

The tallow fatty acids were melted in a large beaker and 50 grams of oil added. The strontium hydrate was then added and while stirring the mixture was heated to a temperature of 450° F. During the heating stage foaming occurred due to the vaporization of water. Toward the end of the foaming stage the remainder of the oil was added. The material, after being heated to 450° F., was set aside to cool to room temperature. The resulting substantially anhydrous product, containing 22.0% by weight of normal strontium soap and having a free acid content (calculated as acetic acid) of 0.03% by weight had a melting point of 300° F.; was semifluid in consistency and too soft for a conventional A. S. T. M. penetration determination.

Example V

A basic strontium soap grease was prepared from the following ingredients:

	Grams
Tallow fatty acids.....	50.0
Acetic acid.....	5.4
Carbon dioxide.....	(1)
Strontium hydrate.....	48.0
SAE 40 grade solvent extracted 90 V. I. oil....	200

¹ Carbon dioxide was bubbled through the grease after the initial saponification and until the free, readily titratable strontium hydroxide content was reduced to substantially zero.

The tallow fatty acids were charged to a large beaker, melted, then mixed with 50 grams of oil and further heated. When the mixture had been heated to a temperature of 180° F. the acetic acid was added and followed by the strontium hydrate. Heating and stirring were continued to effect reaction and partial dehydration and carbon dioxide then bubbled through the mixture for 2 to 3 minute intervals. Heating was continued between carbon dioxide introductions and the remaining oil gradually added. Carbon dioxide was passed through the mixture in this way until analysis showed only a trace of free strontium hydroxide to be present. The grease thickened perceptibly each time carbon dioxide was introduced. Heating was continued with addition of oil to a temperature of 550° F. and the material then set aside to cool to room temperature. After cooling to room temperature the product was worked to a smooth, unctuous grease. The worked, substantially anhydrous product, calculated to contain 21.2% by weight of normal strontium soap, 3.4% of strontium acetate and

2.4% of strontium carbonate and exhibiting a free acid content of 0.1% (calculated as acetic acid), had a melting point of 460° F. and exhibited a consistency as measured by an A. S. T. M. penetration at 77° F. of 298.

Example VI

A basic strontium soap grease was prepared in a similar manner to that described in Example IV, except that glycolic acid was employed in place of acetic acid. A smooth buttery product was obtained which had a consistency as determined by A. S. T. M. penetration at 77° F. of 100.

Example VII

A basic strontium soap grease was prepared in a manner similar to that described in Example IV, except that a portion of the acetic acid was replaced with an equivalent amount of oxalic acid. The resultant substantially anhydrous product had a melting point in excess of 400° F.

Example VIII

A basic strontium soap grease was prepared in a manner similar to that given in Example IV, using 25 grams of tallow, 4.6 grams of propionic acid, 21 grams of strontium hydrate, and 80 grams of naphthenic oil having a Saybolt Universal viscosity of 600 seconds at 100° F. The resulting substantially anhydrous product, calculated to contain 23.7% strontium soap, 6.3% strontium propionate, and having a free alkali content of 0.07%, calculated as strontium hydroxide, had a consistency as measured by A. S. T. M. penetration at 77° F. of 250 and a melting point in excess of 450° F. After standing for several months, there was no evidence of separation of soap and oil.

Other modifications of this invention will be apparent to those skilled in the art.

While the foregoing description of one embodiment of my invention has been made in connection with the preferred use of strontium salts of mineral acids and organic acids of relatively low molecular weight in conjunction with normal strontium soaps and mineral oil to form basic strontium soap greases, I may also form basic strontium soap greases by using other metal salts of the same mineral acids and organic acids of relatively low molecular weight in place of all or part of the corresponding strontium salts. Similarly to the case of strontium salts it is desired to have at least 0.1 equivalent and preferably between 0.2 to 1.0 equivalent or even as high as 3.0 equivalents of the metal salts per equivalent of normal strontium soap. Metal salts useful for this purpose include the salts of sodium, potassium, lithium, calcium, barium, magnesium, aluminum, beryllium, zinc, cadmium, boron, tin, titanium, zirconium, cerium, vanadium, antimony, bismuth, arsenic, copper, molybdenum, caesium, germanium, columbium, chromium, selenium, tellurium, tungsten, manganese, iron, cobalt and nickel.

The incorporation of the metal salt in the grease may be made in accordance with the methods outlined herein for the incorporation of the strontium salts or, if desired, in many cases the metal salts may be produced by adding the metal oxide or hydroxide to a normal strontium soap and subsequently heating to an elevated temperature to effect oxidation of a small proportion of the normal strontium soap to yield low molecular weight acidic products which in turn are neutralized by the metal oxide or hydroxide present and

resulting in the formation of the basic strontium soap lubricants of this invention.

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 strontium soap complex, the latter being a molecular complex containing a ratio of equivalents of strontium to equivalents of saponified high molecular weight organic acids between about 1.1 and 4, and being substantially free from readily titratable excess alkalinity.

2. A lubricating composition comprising mineral oil and strontium soap complex, the latter being a molecular complex containing a ratio of equivalents of strontium 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.

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

5. A lubricating composition according to claim 1, in which the strontium soap complex comprises a normal strontium 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 strontium soap is greater than about 0.1.

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

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

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

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

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

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

12. A lubricating composition according to claim 1, in which the strontium soap complex

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is made by reacting normal strontium soap, basically reacting strontium compound and a low molecular weight organic acid, the amount of said acid being sufficient to neutralize said basically reacting strontium compound.

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

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

15. A lubricating composition according to claim 1, in which the strontium soap complex comprises a mixture of normal strontium soap and strontium acetate.

16. A lubricating composition according to claim 1, in which the strontium soap complex comprises a mixture of normal strontium soap and strontium carbonate.

17. A lubricating composition according to claim 1, in which the strontium soap complex comprises a mixture of normal strontium soap, metal salt of mineral acid and metal salt of low molecular weight fatty acid.

18. A lubricating composition according to claim 1, in which the strontium soap complex comprises a mixture of normal strontium soap, metal carbonate and a metal acetate.

19. A lubricating composition according to claim 1, in which the strontium soap complex comprises a mixture of normal strontium soap, strontium carbonate and strontium acetate.

20. A method of preparing lubricants comprising reacting a saponifiable material with more than one equivalent of a basically reacting strontium compound in the presence of mineral oil and in the presence of oxygen at temperatures

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between approximately 400° F. and 550° F. to yield a strontium soap complex, cooling and adding additional mineral oil, said strontium soap complex being substantially neutral as indicated by titration and containing a ratio of equivalents of strontium to equivalents of saponified high molecular weight organic acids in excess of about 1.1.

21. As a composition of matter, strontium soap complex containing a ratio of equivalents of strontium to equivalents of saponified high molecular weight organic acids between about 1.2 to 1, and about 4 to 1, said soap being substantially free from readily titratable excess alkalinity.

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