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LUBRICATING COMPOSITIONS AND
METHOD OF PREPARATION

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This invention relates to lubricating compositions containing "metal soap complexes" and processes for their production which processes involve treating a mixture of a metal soap and basically reacting metal compound with urea or like complexing agents.

The object of the invention is to obtain all of the benefits in such lubricants and greases as are peculiar to metal soap complexes and to provide processes for producing such greases. A particular object of the invention is to provide a means of preparing lubricants and greases stabilized with metal soap complexes, which method is relatively simple to carry out, is economically feasible and results in the production of metal soap complex lubricants of outstanding quality. Greases produced by methods described herein are unusually stable, 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 are particularly resistant to change in structure and/or body in use or during severe working. The metal soap complexes produced in accordance with this invention generally have unusual thickening effects on lubricating oils even at relatively low concentrations and are compatible with, and may be used to produce stable greases with low V. I. lubricating oils normally used in the production of greases and with relatively high V. I. lubricating oils, which are generally considered to be unsuitable for use in the preparation of stable lubricating greases. Thus, stable greases are formed with both highly paraffinic lubricating oils as well as with the naphthenic lubricating oils.

By the term "metal soap complex" 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 metal 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, saponification reagent 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. The term "equivalents" is used in its chemical sense to mean chemical equivalents.

By the term "normal metal soap" as used in

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

By the terms saponification reagent, base, basic metal compound or basically reacting metal compound as used herein, it is meant to include the various oxides, hydroxides and/or hydrated oxides of those metals which will form salts or soaps with fatty acids, such as stearic acid, oleic acid, etc. Among others the terms saponification reagent, base, basic metal compound or basically reacting metal compound will include the oxides, hydroxides and/or hydrated oxides of the "strongly basic metals," namely, the alkali metals, i. e., lithium, sodium and potassium and the alkaline earth metals, i. e., calcium, strontium and barium and the "weakly basic metals", such as the metals of the right hand column of group II of the periodic table, i. e. beryllium, magnesium, zinc and cadmium, the metals of the right hand column of group III, i. e., aluminum, indium and gallium, the metals of the right hand column of group IV, i. e., lead, tin and germanium, the metals of the right hand column of group I, i. e., silver and copper and the metals of the iron group of group VIII, i. e., iron, cobalt and nickel. The periodic table referred to is that form of Mendeleeff's periodic arrangement of the elements shown in "Handbook of Chemistry and Physics," 25th edition, 1941-1942, pages 308-109.

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, 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, degrass, etc.

According to the present invention valuable lubricating oil addition agents and/or thickening agents, referred to herein as metal soap complexes, which may be used in relatively small amounts in the preparation of crank case lu-

bricating oils having good detergency characteristics and in larger amounts to prepare lubricating greases, may be prepared by treating mixtures of normal soap and excess saponification reagent, in the presence or absence of mineral oil, with a compound which will be referred to herein as a complexing agent. Treatment with the complexing agent at temperatures in the range of 150° F. to 400° F., and preferably in the range of 250° F. to 340° F., results in the formation of an oil-soluble or oil-dispersible metal soap complex free from readily titratable excess alkalinity. The chemistry involved is not simple nor completely understood, but it is observed that in the course of the complexing treatment with complexing agent, the quantity of readily titratable alkalinity is reduced in proportion to the amount of complexing agent employed. If an amount of complexing agent equivalent to the free base is employed all of the basically reacting compound appears to be neutralized as indicated by titration. Moreover, it is observed that the resulting products, which may or may not be completely neutralized with complexing agent, are completely oil dispersible and have improved properties over the normal soap and when neutralized to within the preferred range (which is described later) with complexing agent or with complexing agent and low molecular weight organic acid, all of the desirable characteristics described herein for metal soap complexes are realized. Furthermore it is observed that after treatment of soap-base mixtures with complexing agent, regardless of how much agent is used, the amount of combined metal present in the resulting complex is greater than that present in a normal soap.

During the treatment with complexing agent it is observed that ammonia is evolved. Whether the released ammonia acts in some way to promote the complexing is not known although in view of the complexity of the reactions involved it is possible that the transient presence of ammonia may be beneficial.

Complexing agents which may be employed to produce the metal soap complexes of this invention may be defined as compounds which will react with aqueous sodium hydroxide at temperatures below about 300° F. to convert the sodium hydroxide into sodium carbonate and liberate ammonia. This group of compounds includes ammonium carbonate, ammonium bicarbonate, ammonium sesquicarbonate, ammonium carbamate, ammonium carbamate acid carbonate and urea. Of these compounds urea is the preferred complexing agent. These compounds can be considered to be ammonia derivatives of carbonic acid and where the term "ammonia derivative of carbonic acid" is used in this description and in the claims it is meant to include any and all of the compounds set forth hereabove as complexing agents.

The invention resides in lubricating compositions, especially greases, which contain metal soap complexes, and in the metal soap complexes themselves, which complexes are substantially neutral or substantially free from readily titratable excess alkalinity and are prepared by treating normal soap or partially oxidized normal soap in the presence of free basically reacting metal compound with a complexing agent, such as urea, at temperatures between about 150° F. and about 400° F. The invention resides also in lubricating compositions and particularly greases which contain metal soap complexes which are substan-

tially neutral or substantially free from readily titratable excess alkalinity as well as in the complexes themselves, which complexes are prepared by treating mixtures of normal soap or partially oxidized soap in the presence of basically reacting metal compound with an amount of complexing agent insufficient to neutralize all of the basically reacting compound and thereafter neutralizing the remaining base with a low molecular weight organic acid such as acetic acid.

More particularly the invention resides in mineral oil lubricants containing thickening proportions of metal soap complexes prepared in the manner described where the ratio of equivalents of combined metal to equivalents of higher saponified organic acids is between about 1.2 and 2 although the ratio extends to the upper limit above indicated, i. e., 4 to 1 and may be as low as 1.1 to 1. Particularly stable metal soap complex greases prepared according to this invention have been found to have a ratio within the range of 1.3 to 1 and 1.9 to 1.

The invention includes lubricating compositions containing the metal soap complexes prepared as described herein with high viscosity mineral oils as, for example, mineral oils of 50 to 70 SAE grade or even bright stocks, as well as the lower viscosity mineral lubricating oils as, for example, those of SAE grades 40, 30, 20 or even lower. Good lubricants may also be produced from the lower viscosity "bottoms" fraction obtained by fractionating heavy alkylates obtained from alkylation processes in the manufacture of motor and aviation fuels where the bottoms have a viscosity in the order of that of spray oils or even lower. Moreover, the invention comprises lubricating compositions containing thickening proportions of the metal soap complexes, prepared in the manner set forth, in mineral lubricating oils of substantially any viscosity index from about -20 V. I. to 100 V. I. or even higher. Thus, both naphthenic and paraffinic lubricating oils may be employed as well as acid treated and solvent treated lubricating oils of naphthenic or paraffinic type. Particularly desirable lubricants have been prepared using highly solvent treated Western mineral lubricating oil having a V. I. of about 90. Moreover, highly desirable lubricants have been prepared using a lightly solvent treated Western lubricating oil having a V. I. of about 35.

The invention includes also lubricating compositions consisting of mineral lubricating oil containing metal soap complexes prepared according to the methods outlined herein in which the metal of the metal soap complex is a single metal as well as those complexes in which two or more metals are present in the metal soap complex. Thus, a normal soap of one metal may be complexed with compounds of the same metal, with compounds of a second metal or in some cases compounds of two or more different metals depending upon the desired characteristics of the finished lubricant.

In preparing the lubricants of this invention a normal soap may be converted into a metal soap complex by adding to one equivalent of a normal soap, preferably in the presence of mineral lubricating oil, between about 0.1 equivalent and about 3 equivalents of a basically reacting metal compound and adding to this mixture a complexing agent as for example, urea, in an amount equivalent to all or a part of the basically reacting metal compound. The complexing agent may be added

in the form of an aqueous solution or the dry compound may be used. This mixture is then heated to a temperature in the range of 200° F. to 400° F., and preferably between about 220° F. and 350° F., for a time sufficient to effect the desired complexing which may be only a few minutes or may require as much as several hours depending on the temperatures, the complexing agent and on the metal or metals of the basically reacting agent employed. In case the amount of complexing agent employed is insufficient to neutralize and/or to complex all of the basically reacting compound, part or preferably all of the remaining base may be converted into the salt of a low molecular weight organic acid by treatment with a chemically equivalent amount of the corresponding acid. The resulting mixture is heated to a temperature sufficient to effect dehydration and dispersion of the resulting metal soap complex in the oil. Temperatures in the range of 215° F. to 350° F. may be employed in this step. This heating and complexing may be effected in the presence of part or all of the mineral oil to be employed in the finished lubricant or the complexing reaction may be effected in the absence of mineral oil or in the presence of a volatile thinner, which thinner may be subsequently vaporized to produce a substantially oil-free metal soap complex.

It has been found that the amount of complexing agent to be employed to neutralize a given quantity of basically reacting agent can be determined from a consideration of the molecular weight of the complexing agent and the number of carbon atoms in the complexing agent. Thus, it has been found that one equivalent of basically reacting metal compound is effectively complexed to produce a neutral metal soap complex, i. e., one which is free from readily titratable excess alkalinity, by a weight of complexing agent calculated by dividing the molecular weight of the complexing agent by two times the number of carbon atoms present in the complexing agent. Thus, an equivalent weight of complexing agent, as used in this specification, is the molecular weight of the complexing agent divided by two times the number of carbon atoms in the agent. In the case of urea, ammonium carbonate, ammonium bicarbonate and ammonium carbamate, an equivalent weight is one-half of the molecular weight. An equivalent weight of ammonium carbamate acid carbonate is one-fourth of the molecular weight and the equivalent weight of ammonium sesquicarbonate is one-sixth of the molecular weight.

Low molecular weight organic acids which may be employed, as indicated above, to neutralize free basically reacting metal compounds following treatment with a complexing agent, or if desired, which may be used to neutralize a part of the free basically reacting agent prior to the complexing treatment with complexing agent, include those acids which contain less than about 7 carbon atoms per molecule and which are relatively insoluble in lubricating oil. These include the low molecular weight fatty acids (monocarboxylic), such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, etc., dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, etc., the low molecular weight alkyl and aryl sulfonic acids and such low molecular weight carboxylic acids as glyceric acid, glycolic acid, thioglycolic acid, etc. Of this group of acids the low molecular weight carboxylic acids are preferred and acetic acid is particularly pre-

ferred. When the mixture of normal soap and basically reacting agent is treated with one of the described complexing agents and with a low molecular weight organic acid, as indicated, it is believed that the resulting metal soap complex contains, in addition to any complex formed by reason of treatment with the complexing agent, a metal salt of the low molecular weight organic acid employed which is in some manner solubilized or complexed by the soap or soap complex.

It is preferred that the metal soap complex in lubricants of this invention be substantially neutral although these complexes 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 the 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 adding additional quantities of fatty acid after the substantially neutral metal soap complex has been formed, or may be obtained by adding a larger quantity of low molecular weight carboxylic acid than that required to neutralize the basically reacting metal compound in the formation of the metal soap complex. In order to obtain a free alkali content, additional quantities of basically reacting compound may be added after formation of the substantially neutral metal soap complex, or the excess basically reacting metal compound may be incompletely neutralized during the formation of the complex.

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.

In some instances in the preparation of greases by the methods described herein, granular products are formed which may be converted into desirable lubricants by hydrating and dehydrating the mixture. Thus, a small amount of water, such as between about 1% and about 5%, may be added to the grease at temperatures below about 200° F., and the temperature subsequently raised to about 225° F. to 300° F. with agitation to effect dehydration. The resulting greases have the desirable buttery to slightly fibrous consistency. Usually the hydration-dehydration tech-

nique to produce a finally substantially anhydrous grease is most effective on a slightly acidic metal soap complex grease. Subsequently, the grease can be adjusted to the desired acidity or alkalinity by the addition of a metal oxide or hydroxide or an acid, as the case may be.

In the complexing processes, whether complexing is effected with one of the complexing agents alone, or whether the complexing involves the use of a complexing agent and low molecular weight organic acid or, alternatively, a salt of a low molecular weight organic acid, it is desirable that at least a small percentage of a polar solvent be present in the reaction mixture. The amount of solvent should be at least about 0.1% by weight of the reaction mixture. Preferably this polar solvent should be water, although under some conditions complex formation proceeds more readily in the presence of water and glycerin, water and glycol or water with some other hydroxy or poly-hydroxy organic compound such as ethyl alcohol, diethylene glycol and the like. Preferably the proportion of polar solvent should be in the range of 0.5% to about 4.0% by weight of the reacting mass although quantities of 10% or more of the polar solvent can be employed. The effect of the presence of polar solvent in assisting the complex formation is not understood, but it has been observed that complex formation occurs more rapidly and/or takes place at lower temperatures in the presence of such solvent.

In the preferred method for forming metal soap complex greases of this invention a normal metal soap is dissolved in all or only a portion of the mineral oil to be used, and to this oil solution of soap is added an amount of free basically reacting metal compound between 0.1 and 3.0 equivalents, and preferably between 0.2 and 1.0 equivalent per equivalent of normal soap. To this oil solution of soap and free base is added an amount of urea sufficient to neutralize between about 25% and 75% of the free basically reacting metal compound. The urea may be added in the form of an aqueous solution or the dry urea may be employed. The mixture is then agitated and heated to a temperature in the range of 250° F. to 340° F. When the neutralization with urea is substantially complete the batch is cooled to 200° F. or below and an amount of acetic acid equivalent to the remaining unreacted basically reacting metal compound is then added while continuing the agitation. The resulting substantially neutral product may be again heated with agitation, thereby boiling off or evaporating all or a portion of the water present in the mixture. Additional oil can be added during or after the removal of the water, 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.

Although in the above method the complexing agent is added first and followed by the neutralization of the remaining free base with low molecular weight organic acid, it is within the scope of the invention to reverse the sequence of addition, adding acetic acid, for example, to the mixture of soap, oil and free base at a temperature of 200° F. or lower to neutralize a part, i. e. 25% to 75% of the free base and subsequently add the urea or other complexing agent in an amount equivalent to the remaining free base.

The mixture is then heated to a temperature preferably within the range of 250° F. to 340° F. to effect reaction of the complexing agent and the free base.

In preparing the lubricants of this invention it is sometimes feasible to add the complexing agent such as urea and the low molecular weight organic acid such as acetic acid at the same time, heating the reaction mixture to the temperatures indicated to effect complexing and dehydration.

As a further modification of the preferred method, sufficient complexing agent is employed to completely neutralize the basically reacting compound present and an aqueous solution or dispersion of a metal salt of a low molecular weight organic acid, such as a metal acetate, may be added to the reaction mixture either before or after treatment with the complexing agent to produce a desirable metal soap complex. In order to effect complexing of the metal salt the mixture is heated to a temperature sufficient to vaporize a part or all of the water added with the salt.

In another preferred method, sufficient urea may be added to a mixture comprising normal metal soap and basically reacting metal compound in the presence or absence of mineral oil to neutralize substantially all of the basically reacting metal compound. The resulting metal soap complex is particularly desirable in the case of those metals or combinations of metals which form complexes having unusually low oil solubility. Apparently with certain metals, at least, the metal soap complexes prepared in this manner are appreciably more oil-soluble than those complexes of the same metal or metals containing in addition, low molecular weight organic acid salts.

It is within the scope of this invention to employ in place of the normal metal soap above described, a soap mixture prepared by oxidizing a normal metal soap in the presence of free basically reacting metal compound. Thus, one equivalent of saponifiable material may be reacted with more than one equivalent, as for example 1.1 to 4 equivalents, of a basically reacting metal compound at elevated temperatures in the presence of oxygen until all or at least a part of the basically reacting metal compound which was not utilized in forming the normal soap has been converted into salts of acidic oxidation products. This oxidation reaction may be effected at temperatures between about 200° F. and 600° F., preferably in the presence of a small amount of polar solvent such as the amount indicated to be desirable for complex formation. After at least some of the excess basically reacting compound has been neutralized the oxidation reaction is arrested by reducing the temperature to a point below about 300° F. and the remaining free basically reacting metal compound may then be complexed by adding one of the complexing agents described, such as urea, and the batch reheated if necessary to effect neutralization of the remaining base and complexing. In case the oxidation reaction is carried to such a degree that substantially all of the free basically reacting agent has been converted to the corresponding salts of acids produced during the oxidation, an additional quantity of basically reacting agent is added to the oxidation product and complexing effected as above described with one of the complexing agents. Moreover, as indicated above, the amount of complexing agent employed in either instance

may be that amount required to neutralize all of the remaining basically reacting compound present or may be sufficient to neutralize only a part of the base present, the remaining base being converted into metal salt of a low molecular weight organic acid by adding an equivalent amount of the corresponding acid. In any case after neutralization whether by the use of complexing agent alone or together with acidification, the reaction mixture is agitated and heated to a temperature sufficient to effect dehydration and complexing.

In the preceding methods employing oxidation of normal soap in the presence of basically reacting agent, it is desirable that at least a part of the oil to be used in the preparation of the finished lubricant be present during the oxidation and subsequent steps. Additional oil may be added at any time during the process or may be added after complexing has been completed to produce the finished lubricant.

It is to be understood that all of the complexing agents disclosed may be employed in the processes which have been described under the conditions set forth to produce satisfactory metal soap complexes which are useful in the preparation of lubricating oils and greases having desirable characteristics. However, it is to be pointed out that variations do exist in the efficiency of the various agents and in the character of the resulting products. Urea appears to produce particularly valuable metal soap complexes.

It has been indicated that the processes of this invention are applicable to the production of metal soap complexes, lubricants and greases using soaps of various metals and basically reacting agents of the same metals or different metals. From this it is not to be understood that greases prepared from all of the various metals and combinations of metals are equivalent or have the desired characteristics to the same degree. In fact, the complexes formed from various basic metal compounds with a given normal metal soap vary over a wide range as regards their respective solubilities in a given mineral lubricating oil. Particularly preferred greases are those prepared from barium soaps and barium hydrate complexed by treatment with a complexing agent and a low molecular weight organic acid. However, the other alkaline earth metals and magnesium may be employed in the preparation of desirable metal soap complexes and greases using single metals or using combinations of these metals. Thus, a barium soap may be employed with basic compounds of calcium, magnesium or strontium to produce metal soap complexes useful in the preparation of high quality lubricants. Moreover, other combinations of metals have been found to produce highly desirable metal soap complexes and in general when two or more metals are to be employed in the preparation of a complex it is possible to use the normal metal soap of either of the two metals and a basically reacting compound of the other metal. In some cases, and for certain purposes it is desirable to select a particular metal to be used in the form of a soap and a particular second metal to be used in the form of a basically reacting compound for subsequent complexing. This latter situation exists particularly in connection with the alkali metals. In this case it is usually desirable to employ a polyvalent metal soap and an alkali metal hydroxide in the preparation of mixed polyvalent metal-alkali metal soap complexes.

It is to be noted that the greases of this inven-

tion can usually be produced as anhydrous or 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%. This water can be incorporated in any of the several stages in the process of making the grease as will be obvious to one skilled in the art. Thus, if the grease has less than the desired amount of water, the required amount of 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 during the addition of oil and the excess water subsequently removed by increasing the temperature of the grease to a temperature of 220° F. or as high as 300° F., if necessary, and then cooling after the desired water content has been reached.

The amount of metal soap complex to be incorporated in the greases of this invention will generally be between about 5% and about 50% although concentrations as low as about 2% in some cases and as high as 75% may be desirable for certain special applications.

Metal soap complexes of this invention may also be used in relatively small proportions to produce liquid greases and fluid lubricants such as lubricating oils for internal combustion engines. In such applications, soap concentrations are usually below about 5% and are normally in the range of 0.2% to 1.5% or 2.0%. With certain saponifiable materials, metal soap complexes and mineral oils, it is possible to produce fluid lubricants containing 10% by weight of the metal soap complex or even more.

Other materials may be added to the lubricating compositions of this invention, such other materials including water, alcohols and other solvents, anti-oxidants, fillers, etc., as desired. Moreover, other materials may be substituted for a part or all of the mineral lubricating oil, such other materials including asphalt, petrolatum, solvent extracts from lubricating oils, and the like.

The following examples are given as illustrations of the invention:

Example I

A barium soap complex grease is prepared from the following ingredients:

	Kilograms
Prime tallow	7.0
Tallow fatty acids	21.0
Urea	1.5
Acetic acid (80%)	1.88
Barium hydrate ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$)	28.5
SAE 40 naphthenic lubricating oil	82.2

The prime tallow, tallow fatty acids, 14.0 kg. of the mineral oil and the barium hydrate are charged to a steam jacketed grease kettle of about 1 barrel capacity equipped with means for agitation and heated to about 235° F. with agitation. At this time the urea and an additional 14.0 kg. of the oil are added and the mixture agitated and heated to 300° F. for a period of about 1½ hours. The mixture is cooled to 200° F. and about 0.5 kg. of water is added. The acetic acid is then added and the temperature raised to 250° F.-275° F. while continuing the agitation for about 1 hour. The remainder of the lubricating oil is added while cooling the grease to 200° F., after which 0.5 kg. of water is added to hydrate the grease

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and dehydration subsequently effected by raising the temperature to 285° F. The finished grease contains about 34.1% metal soap complex having a ratio of equivalents of combined barium to equivalents of saponified higher molecular weight acids of about 1.75 to 1. The product is unctuous and has a slightly fibrous structure. The unworked ASTM penetration at 77° F. is 272.

Example II

A barium soap complex grease prepared as in Example I, except that 2.4 kg. of ammonium carbonate is substituted for the urea, is substantially identical with that of Example I.

Example III

A barium soap complex grease prepared according to the procedure of Example I, except that 2 kg. of ammonium carbamate is substituted for the urea, is substantially the same as the one prepared using urea.

Example IV

A barium soap complex grease prepared following the procedure outlined in Example I, except that in place of the acetic acid, an equivalent amount of propionic acid is employed, has a greater penetration, is slightly less fibrous and appears more feathery than the corresponding acetated grease. This grease has a melting point over 400° F.

Example V

A barium soap complex grease prepared according to the procedure of Example I, except that one-half of the acetic acid is substituted for by an equivalent amount of oxalic acid, is similar in appearance, consistency and structure to the grease of Example I.

Example VI

A strontium soap complex grease prepared following the procedure of Example I, except that 24.3 kg. of strontium hydrate is substituted for the barium hydrate, is a smooth grease and slightly less fibrous than the corresponding barium soap complex grease. The product, which is substantially anhydrous and neutral, has a ratio of equivalents of combined strontium to saponified higher molecular weight acids of 1.75 to 1.

Example VII

A barium soap complex grease is prepared from the following ingredients:

	Kilograms
Prime tallow	4.2
Tallow fatty acids	23.8
Urea	1.5
Acetic acid (80%)	1.83
Barium hydrate ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$)	28.8
SAE 40 naphthenic lubricating oil	130.0

The prime tallow, tallow fatty acid, 14 kg. of the mineral oil and the barium hydrate are charged to a grease kettle such as that referred to in Example I and the mixture heated with agitation to about 235° F. to effect saponification. After cooling to 190° F. the acetic acid and urea are added to the saponified mixture and agitating and heating continued for about 1¼ hours after the temperature reaches 300° F. with a maximum temperature of about 340° F. The resulting mixture is cooled to about 200° F. while adding a second 14 kg. portion of the lubricating oil and hydrated by adding 5 kg. of water. Dehydration is effected by heating to about 300° F. This product is then reduced with the remaining lubri-

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cating oil while gradually cooling the batch to 200° F. to give a smooth, slightly fibrous grease.

The finished grease contains 24.8% by weight of metal soap complex and has a ratio of equivalents of combined metal to equivalents of saponified higher molecular weight acids of 1.75 to 1. This product has an unworked ASTM penetration at 77° F. of 267.

Example VIII

A calcium soap complex grease prepared according to the procedure of Example VII, except that the barium hydrate is replaced by 6.77 kg. of calcium hydroxide is less fibrous than the barium soap complex grease. This product is substantially anhydrous and neutral and has a ratio of equivalents of combined calcium to saponified higher molecular weight acids is 1.75 to 1.

Example IX

A magnesium soap complex grease is prepared in a manner similar to the procedure of Example VII except that an equivalent amount of magnesium hydroxide is substituted for the barium hydrate.

Example X

A barium soap complex grease is prepared from the following ingredients:

	Kilograms
Prime tallow	0.70
Tallow fatty acids	2.10
Urea	0.225
Barium hydrate ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$)	2.850
SAE 30 paraffinic mineral lubricating oil, 100 V. I.	8.400

The prime tallow, tallow fatty acids, 14 kg. of the lubricating oil and the barium hydrate are charged to a 1 barrel grease kettle, such as was described in Example I, and the mixture heated with agitation to about 235° F. to effect saponification. After saponification is complete the urea is added and the mixture further heated to 300° F. and maintained between about 300° F. and 350° F. for two hours. The resulting, substantially neutral product is reduced with the remainder of the lubricating oil and cooled to about 200° F. The grease at this stage is substantially anhydrous and has the desirable features which are typical of the metal soap complex greases of this invention.

The appearance and structure of the grease is improved by adding about 0.05% of water and agitating the grease while gradually raising the temperature to 285° F. to effect dehydration. The product is cooled while continuing the agitation. The final grease which is smooth, free from granulation and has a buttery structure, has a ratio of equivalents of combined barium to saponified higher molecular weight acids of 2.0 to 1.

Example XI

A magnesium soap complex grease is prepared using the procedure of Example X with the following ingredients:

	Kilograms
Prime tallow	14.0
Tallow fatty acids	14.0
Urea	3.0
Magnesium hydroxide	6.1
SAE 30 solvent treated Western Lubricating oil of 90 V. I.	110.0

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The product after hydrating, dehydrating and cooling is a smooth unctuous grease. It is substantially neutral and contains a ratio of equivalents of combined magnesium to saponified higher molecular weight acids of 2 to 1.

Example XII

A calcium soap complex lubricant is prepared from the following ingredients:

	Kilograms
Prime tallow	1.40
Tallow fatty acids	1.40
Urea	0.30
Calcium hydroxide	0.775
SAE 30 solvent treated Western lubricating oil of 90 V. I.	11.0

The procedure employed is the same as described in Example X with the exception that final hydration and dehydration is avoided. In this case the product which contains about 21% of calcium soap complex is a low melting point product, of buttery texture. This substantially anhydrous product contains a ratio of equivalents of combined calcium to saponified higher molecular weight acids of 2 to 1.

Example XIII

A calcium-sodium soap complex lubricant is prepared from the following ingredients:

	Grams
Prime tallow	450
Urea	24.3
Acetic acid (80%)	34.0
Calcium oxide	51.5
Sodium hydroxide	42
SAE 30 naphthenic lubricating oil, 35 V. I.	1200

The tallow together with 225 g. of the lubricating oil is saponified with the calcium oxide (after slaking) to form a normal calcium soap. After saponification is complete the mixture is cooled and diluted with another 225 g. portion of the lubricating oil. To the cooled, diluted soap is added the sodium hydroxide and urea and the mixture reheated to 300° F.-350° F. for a period of 45 minutes. After cooling to 200° F. the acetic acid is added to complete the neutralization of sodium hydroxide. The resulting grease contains 1.9 equivalents of combined metal per equivalent of saponified high molecular weight organic acids, is substantially neutral as indicated by titration, and has a melting point of 275° F.

Example XIV

A calcium-barium soap complex lubricant is prepared according to the procedure of Example XII except that the sodium hydroxide is replaced with 221 g. of barium hydrate. The resulting grease is a non-fibrous, buttery product having a ratio of equivalents of combined metal to saponified higher molecular weight organic acids of about 2.1 to 1.

Example XV

An aluminum-barium soap complex grease is prepared using the following ingredients:

	Grams
Aluminum stearate	300
Urea	15
Acetic acid, 80%	19
Barium hydrate	160
SAE 30 naphthenic type lubricating oil, 35 V. I.	600

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The aluminum stearate is dissolved in about one-half of the lubricating oil, the barium hydrate, urea and acetic acid are then added with constant agitation. The reaction mixture is heated to a temperature in the range of about 300° F. to 350° F. for a period of two hours and the remainder of the lubricating oil is then slowly added as the batch is cooled to about 200° F. About 0.05% of water is added to improve the body and smoothness of the grease. This product contains about 3.9% of metal soap complex.

Example XVI

An aluminum-sodium soap complex grease is prepared using following ingredients:

	Grams
Aluminum stearate	215
Urea	10.8
Acetic acid, 80%	13.6
Sodium hydroxide	21.5
SAE 30 naphthenic lubricating oil, 35 V. I.	500

The procedure of Example XV is employed except that sodium hydroxide, in water solution, is used in place of the barium hydrate and the product is not hydrated. The resulting grease is anhydrous and nearly fluid at room temperature.

Example XVII

A calcium-strontium soap complex grease is prepared by adding to 16.7 kg. of a conventional cup grease containing 18% by weight of calcium tallow soap, 0.66 kg. of strontium hydrate and 0.15 kg. of urea, heating the mixture to a temperature of 325° F. for about two hours, cooling the reaction mixture to about 225° F. and adding thereto 0.43 kg. of strontium acetate dissolved in 1.0 kg. of water. This mixture is heated to a temperature of 350° F. and cooled. The cooled grease is worked to give a smooth transparent grease which is substantially neutral and contains about 21.6% of metal soap complex with a ratio of combined metal to saponified higher molecular weight acids of about 1.9 to 1.

Example XVIII

A barium soap complex grease is prepared from the following ingredients:

	Grams
Prime tallow	4200
Urea	82
Barium hydrate	4800
SAE 30 naphthenic lubricating oil, 35 V. I.	12,500

The prime tallow, barium hydrate and 2500 grams of the lubricating oil is charged to a grease kettle and heated to 230° F. An additional 2500 grams of oil is then added slowly and the mixture heated to 300° F. while vigorously agitating to effect contact of the mixture with air. Reaction at this temperature is allowed to proceed until the free Ba(OH)₂ content is reduced to 2%. The product is cooled, hydrated with about 0.05% water and the urea is then added at a temperature of 235° F. and the temperature increased to 300° F.-350° F. for about 1.5 hours. The resulting grease is cooled, hydrated and dehydrated and then cooled to about 210° F. while adding the remainder of the mineral lubricating oil. This product contains about 24.7% soap, an ASTM worked penetration at 77° F. of 264 and is substantially neutral as indicated by titration.

Example XIX

A barium-sodium soap complex grease is prepared according to the procedure of Example XVIII except that sodium hydroxide is substituted for the barium hydrate. The following ingredients are employed:

	Grams
Prime tallow -----	70
Tallow fatty acids -----	210
Urea -----	15
Barium hydrate -----	175
Sodium hydroxide, 98% -----	40
SAE 30 naphthenic lubricating oil -----	1525

The resulting grease is slightly feathery, has an ASTM unworked penetration at 77° F. of 220 and a melting point of about 300° F.

Example XX

An oil-free metal soap complex is prepared by saponifying 280 g. of prime tallow with 158 g. of barium hydrate. To the resulting normal soap is added 158 g. of barium hydrate and 30 g. of urea together with 20 g. of water and the mixture heated to 280° F. to 300° F. for 1½ hours. The resulting mixture, which solidifies as it cools, is a barium soap complex which is readily dispersed in oil to produce greases.

Example XXI

An oil-free metal soap complex is prepared by saponifying 280 g. of oleic acid with 63 g. of calcium hydroxide and 10 g. of water. To the saponified mixture which still contains free calcium hydroxide is added 800 g. of petroleum thinner boiling in the range of 250° F. to 300° F., 12 g. of urea, and 18 g. of acetic acid. The resulting mixture is refluxed for four hours and the thinner and water are then removed by evaporation. The resulting calcium soap complex is substantially neutral and contains a ratio of equivalents of combined calcium to equivalents of higher molecular weight acids of 1.7 to 1.

Example XXII

A mixture of 50 grams of tallow fatty acids, 5 grams of glycerol, 9.5 grams of calcium oxide and 50.0 grams of water is heated to 240° F. with agitation to effect saponification. The resulting partially dehydrated product is heated to 300° F. to 375° F. for one hour in contact with air and with the constant agitation to effect partial oxidation. To the product are added 2.4 g. of urea and 5 g. of water and the mixture held at a temperature of 300° F. for about 1.5 hours and then cooled. The cooled mixture is an anhydrous oil-free solid calcium soap complex.

A grease is prepared by dispersing about 20% by weight of the calcium soap complex in SAE 40 naphthenic lubricating oil of 25 V. I. at a temperature of about 400° F. This grease is substantially neutral as indicated by titration and is anhydrous. The ratio of equivalents of combined calcium to equivalents of higher molecular weight acids is about 1.9 to 1.

The foregoing description of our invention is not to be taken as limiting our 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.

We claim:

1. A method of producing a metal soap complex comprising reacting a mixture of metal soap and between about 0.1 and 3 equivalents of basically reacting metal compound per equivalent

of metal soap with an amount of complexing agent equivalent to the basically reacting metal compound to produce a substantially neutral metal soap complex, said complexing agent being an ammonia derivative of carbonic acid.

2. A method of producing a lubricating composition comprising mixing mineral oil, metal soap, between 0.1 and 3 equivalents of basically reacting metal compound per equivalent of metal soap, water and a complexing agent and heating the mixture to produce a substantially neutral product, said complexing agent being an ammonia derivative of carbonic acid.

3. A method according to claim 2 in which the temperature of heating to produce a substantially neutral product is within the range of about 150° F. to 400° F.

4. A method according to claim 2 in which the metal of the metal soap is different from the metal of the basically reacting metal compound.

5. A method according to claim 2 in which the metal of the metal soap and the metal of the basically reacting metal compound are alkaline earth metals.

6. A method according to claim 2 in which the complexing agent is urea.

7. A method of producing a lubricating composition comprising reacting a mixture of mineral oil, metal soap and 0.1 to 3 equivalents of free basically reacting metal compound per equivalent of metal soap with an amount of a complexing agent sufficient to neutralize a part of said free basically reacting metal compound, adding to the resulting mixture an amount of a low molecular weight organic acid sufficient to complete the neutralization of the free basically reacting metal compound and dispersing the resulting substantially neutral product in mineral oil, said complexing agent being an ammonia derivative of carbonic acid.

8. A method of producing a lubricating composition comprising reacting a mixture of mineral oil, metal soap, and 0.1 to 3 equivalents of free basically reacting metal compound per equivalent of metal soap with an amount of a low molecular weight organic acid sufficient to neutralize a part of said free basically reacting metal compound, adding to the resulting mixture an amount of a complexing agent sufficient to neutralize the remaining free basically reacting metal compound, heating the mixture to a temperature in the range of about 150° F. to 400° F. to effect reaction with said complexing agent and dispersing the resulting substantially neutral product in mineral oil, said complexing agent being an ammonia derivative of carbonic acid.

9. A method of producing a lubricating composition comprising saponifying one equivalent of a saponifiable material with between 1.1 and 4 equivalents of a basic metal compound, adding to the saponified mixture a sufficient amount of a complexing agent to neutralize the unreacted basic metal compound to produce a substantially neutral product, and dispersing the resulting substantially neutral product in mineral oil, said complexing agent being an ammonia derivative of carbonic acid.

10. A method of producing a lubricating composition comprising saponifying one equivalent of a saponifiable material with between 1.1 and 4 equivalents of a basic metal compound, heating the saponified mixture with a sufficient amount of a complexing agent to neutralize a portion of the unreacted basic metal compound and adding to the partially neutralized mixture a sufficient amount of a low molecular weight organic acid to

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neutralize the remaining free basically reacting metal compound and dispersing the resulting substantially neutral product in mineral oil, said complexing agent being an ammonia derivative of carbonic acid.

11. A method according to claim 9 in which the metal of the basic metal compound is an alkaline earth metal.

12. A method according to claim 9 in which the metal of the basic metal compound is barium.

13. A method according to claim 9 in which the metal of the basic metal compound is strontium.

14. A method of producing a metal soap complex comprising reacting a mixture of metal soap and 0.1 to 3 equivalents of free basically reacting metal compound per equivalent of metal soap with an amount of a complexing agent to neutralize a part of said free basically reacting metal compound, adding to the reaction mixture an amount of a low molecular weight organic acid sufficient to neutralize the remaining free basically reacting metal compound thereby producing a substantially neutral metal soap complex, said complexing agent being an ammonia derivative of carbonic acid.

15. A method of producing a lubricating composition comprising oxidizing a metal soap with a gas containing free oxygen in the presence of a free basic metal compound to produce acidic oxidation products in quantities sufficient to partially neutralize said free basic metal compound thereby producing salts of said acidic ox-

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5 dation products, reacting the resulting mixture with a sufficient quantity of a complexing agent to neutralize the remaining free basic metal compound and dispersing the resulting substantially neutral product in mineral oil, said complexing agent being an ammonia derivative of carbonic acid.

16. A method according to claim 2 in which the complexing agent is ammonium carbonate.

17. A method according to claim 2 in which the complexing agent is ammonium carbamate.

18. A method according to claim 2 in which the metal soap is a polyvalent metal soap and the basically reacting metal compound is a basically reacting alkali metal compound.

19. A method according to claim 18 in which the polyvalent metal soap is a barium soap.

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