

UNITED STATES PATENT OFFICE

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LUBRICATING COMPOSITION

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This invention relates to lubricating compositions containing complex basic barium soaps and has special reference to complex barium soap greases.

The object of the invention is to obtain all the benefits of such lubricants and greases as are peculiar to complex barium soaps. Complex barium soaps produce stable greases which have excellent melting point and penetration characteristics, do not require hydration, and have exceptional resistance to deterioration by the action of heat and by the action of moisture. Another object of this invention is to provide processes for the manufacture of complex barium soap lubricants.

Complex barium soaps as used herein include products which are substantially neutral or substantially free from readily titratable excess alkalinity, at least beyond a relatively small amount, these products comprising a complex of a normal barium soap with a barium salt. The number of mols of barium salt combined with each mol of barium soap should be greater than 0.1 and, depending upon the particular saponifiable material and upon the characteristics of the mineral oil employed, it is preferred that the number of mols of barium salt per mol of normal barium soap be between about 0.2 and 1.0, but it may be as high as 2.0 or even as high as 3.0.

Normal barium soaps as used herein include those products which result when one equivalent of barium hydroxide or other basically reacting barium compound is reacted with one equivalent of a saponifiable material to form a soap, said soap being the normal barium salt of the high molecular weight organic acids present as such or desirable by saponification from the saponifiable material.

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

The present invention resides in lubricating compositions, especially greases which contain complex barium 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

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Diesel engine lubricating oils containing small proportions of complex basic soaps, it includes more particularly the use of such complex barium soaps in proportions to thicken lubricating oils appreciably for the purpose of producing liquid greases or solid greases of varying consistencies. More particularly the invention resides in mineral oil lubricants containing thickening proportions of complex barium soaps where the molal ratio of barium salt to normal barium soap is between about 0.2 and 1.0, although it extends to the upper limit above indicated, i. e., 3.0 and may be as low as 0.1. Especially stable complex barium soap greases have been found to have a molal ratio within the range of 0.3 to 0.9. The invention also comprises the method of making such lubricants.

The invention also includes the use of basic soaps to produce lubricants employing high viscosity mineral oils, e. g., 50 or 70 SAE grade or even bright stocks as well as lower viscosity mineral oils, e. g., 10 or 20 SAE grade. These mineral oils can be either of the Pennsylvania type which have a viscosity index of 90 or higher, or the Mid-Continent type or even of the naphthenic type which have a viscosity index of 30 or lower. Greases of unusually good water resistance have been prepared from oils containing as much as 25% by weight of asphalt or extracts derived from lubricating oil distillates by treatment with phenol, furfural, etc.

I have discovered that under appropriate conditions it is possible to form a complex having unique solubility characteristics in mineral lubricating oils by reacting one mol of a normal barium soap with more than about 0.1 mol of a barium salt. By the term "barium salt" it is meant to include preferably the simple reaction product resulting from the combination of one equivalent of barium hydroxide with one equivalent of a mineral acid such as sulfuric acid, hydrochloric acid, orthophosphoric acid, pyrophosphoric acid, sulfurous acid, carbonic acid, boric acid, thiosulfuric acid or of an organic acid of relatively low molecular weight such as the 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, thioglycollic, etc., acids, and the low molecular weight phenolic and thiophenolic compounds such as phenol, cresol, thiophenol, etc. However, I may

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also employ acidic or basic salts in which one equivalent of barium hydroxide has been reacted with more or less than one equivalent of a mineral acid or low molecular weight organic acid. Preferably, the barium salt should be barium acetate or barium carbonate or a mixture of barium acetate and barium carbonate.

Desirably the complex barium soap is substantially neutral or free from relatively titratable excess alkalinity. By the terms "substantially neutral" or "substantially free from readily titratable excess alkalinity" as used in this invention, are meant to include greases having a free acid or free alkali content less than about the equivalent of 5.0 mg. of KOH per gram of soap present. While it is preferred that the greases of this invention be substantially neutral, under some conditions they may desirably contain a small amount of free acidity or alkalinity. For example, the finished greases may have a free alkali content, calculated as $\text{Ba}(\text{OH})_2$, 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. Greases having a desired free acid or free barium hydroxide content can be produced by controlling the ratio of acidic materials to basically reacting compounds as will be obvious to one skilled in the art.

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 $\text{Ba}(\text{OH})_2$; 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.

While I do not wish to be limited by the theories advanced herein, it appears, however, that under the conditions as disclosed in this invention, it is possible for normal barium soap to form an "association complex" with a barium salt, this complex acting in many respects as a single chemical component. For example, this complex has a different solubility in lubricating oil than either the normal barium soap or the barium salt of which it is composed. Further, although a given barium salt when added to a normal barium soap grease as a filler, may be readily extractable with water, the same barium salt combined with the normal barium soap in the form of a complex barium soap of the present invention is extractable either only with difficulty or not at all. As another indication of the novelty of my complex barium soap greases, atten-

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tion should be called to the fact that whereas barium salts are usually relatively insoluble in mineral oils and when added as fillers to conventional normal soap greases, the latter are opaque and the salts can be largely removed by passing through a fine mesh screen, my greases are relatively transparent or translucent in appearance and none of the salt is removable by mechanical means.

It is not meant to intimate that any given barium salt is the full equivalent of any other barium salt for modifying the characteristics of a dispersion of normal barium soap in lubricating oil. In fact the complexes of various barium salts with a given normal barium soap vary over a wide range as regards their respective solubilities in a given mineral lubricating oil. For example, a normal barium stearate-barium carbonate complex is more soluble in a given mineral oil than is a normal barium stearate-barium formate complex. Likewise, the latter complex appears to be more soluble than one formed from normal barium stearate and barium acetate. Complexes of a given normal barium soap with certain barium 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 barium soap with different barium 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 to be used will depend upon the relative solubilities of the two complexes and can be readily determined by one skilled in the greasemaking 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 saponifiable materials and barium salts the greases produced by the processes of the present invention have a granular appearance, but by employing the hydration-dehydration technique, products of smooth buttery texture are obtained often accompanied by an increase in consistency and melting point. Usually the hydration-dehydration technique to produce a final substantially anhydrous grease is most effective on a slightly acidic complex barium soap grease. Subsequently the grease can be adjusted to the desired acidity or alkalinity by the addition of barium hydroxide or acid, as the case may be. 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.

Although preferably the complex barium soap greases of this invention are produced as sub-

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stantially anhydrous products under some conditions a slight water content such as 0.01% to 0.05% or even as high as 0.3% may be desirable for some purposes. Incorporation of this water can be accomplished at any of a number of stages in the preparation of the grease as will be obvious to one skilled in the art. For example, after hydrating the grease as described above, the subsequent dehydration can be stopped at a point which will give the water content required in the finished product or after complete dehydration the desired quantities of water can be added and incorporated in the grease.

In order for the desired 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 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 complex formation proceeds more readily in the presence of a mixture of water and glycerine, water and glycol or 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 that anhydrous normal barium soap when heated with anhydrous barium acetate in the presence of oil at various temperatures failed to form the complex barium soap greases of my invention and in fact the barium acetate remained undissolved. On the other hand, when the same mixture to which had been added 5% of water was mixed and subsequently heated to dehydrate the mixture, the complex barium soap was formed and there was no evidence of any free barium acetate in the finished grease.

One of the preferred methods of forming the complex barium soap lubricants of the present invention is to charge to a kettle equipped with means for heating, cooling, and agitation, an amount of barium hydrate ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) equivalent to the number of mols of barium soap plus barium salt desired in the finished product. Subsequently the acid or acids, whose barium salt is desired in the finished greases is added in an amount equivalent to that desired in the complex barium soap. After heating and agitating to effect reaction of this acid with the barium hydroxide the saponifiable material is added in an amount just sufficient to react with the remaining barium hydroxide. Desirably the saponifiable material is mixed with between about one-fourth and twice its weight of the mineral oil to be present in the finished lubricant. After the introduction of the saponifiable material, heating and agitation is continued to effect saponification and subsequently dehydration of the complex barium soap. After dehydration has been completed or even during the dehydration step, additional mineral oil may be added. Finally, the lubricant is heated to a temperature of between about 250° F. and 350° F. or higher to complete dehydration and obtain the desired characteristics and then cooled to approximately 200° F. If desired, a small proportion of water can be added at this time and subsequently removed as described under the hydration-dehydration technique. Finally, the lubricant is

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cooled to room temperature, and if a grease, worked in the cold and drawn into packages. Heating is preferably conducted at atmospheric pressure in an open bottle, however, the heating and reaction may be carried out in a closed kettle under superatmospheric pressure.

Another preferred method of forming the complex barium soap lubricants of this invention comprises mixing the saponifiable material, a small amount of mineral oil and the acid, or acids, whose barium salt is desired in the complex barium soap. Subsequently, barium hydrate in an amount equivalent to the saponifiable material and acid is added to the mixture and the material heated and agitated to effect reaction and dehydration. During the dehydration stage additional oil may be added or all of the remaining oil required may be added subsequent to the dehydration stage. The lubricant is finally heated to a temperature of between about 250–350° F. or even as high as 550° F., subsequently cooled to room temperature and if a grease, worked in the cold to give the final product. The hydration-dehydration technique may be employed at any of several stages, as will be obvious to one skilled in the art.

It is also possible to first form a normal barium soap grease and subsequently add barium hydrate, followed by an equivalent amount of the acid whose barium salt it is desired to complex with the normal barium soap. Also it is possible to produce a complex barium soap lubricant by adding a barium salt dissolved, or at least partially dissolved, in water or other appropriate polar solvent as described hereinabove to a normal barium soap grease and subsequently heat to effect formation of the complex barium soap.

The formation of the complex barium soap lubricants of this invention generally require moderately high temperatures, preferably in the range of about 225°–325° F. However, under some conditions it is desirable that the complex barium soap lubricants of this invention be heated to temperatures as high as 400° F. or even 550° F. prior to cooling and working in the cold. In forming the normal barium soaps and barium salts by reacting a saponifiable material or an acidic material with a basically reacting compound, the base is added preferably as the hydroxide, $\text{Ba}(\text{OH})_2$, or as barium hydrate, although in some instances barium oxide or other basically reacting barium compound 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 complex barium soap formation is preferably carried out in the presence of part of the lubricating oil to be used in the finished lubricant, although inert low-boiling solvents may be used under pressure and subsequently evaporated to leave a pure complex barium soap residue. The powder can then be dispersed in a mineral oil to form a complex barium soap lubricant of the present invention.

The amount of complex barium 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.

Complex barium 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%.

Materials other than complex barium soaps may also be added to the lubricating compositions of this invention, such as water, alcohols, and other solvents, oxidation inhibitor, fillers, etc., as desired. Additions of petrolatum and solvent extracts from lubricating oil stocks have been helpful in some instances. Oxidation inhibitors which may be added to the grease include phenyl alpha naphthylamine, tetramethyl diamino diphenyl methane, benzidine, etc., and the amount thereof vary from about 0.001% to about 1.0% of the finished grease.

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

EXAMPLE I

The following ingredients were charged to a steam jacketed grease kettle of about 1-barrel capacity equipped with means for agitation:

	Pounds
Tallow fatty acids (saponification number=208 mg. KOH per gram)-----	50
Naphthenic type oil (viscosity=350 Saybolt Universal seconds at 100° F.)-----	25

These materials were heated to approximately 180° F. and mixed to form a homogeneous solution.

Separately, 25 pounds of barium hydrate, 20 pounds of water, and 8 pounds of glacial acetic acid were mixed, then added to the kettle and followed by 27 pounds of barium hydrate, the temperature in the kettle being between 180 and 200° F.

The kettle ingredients were continuously agitated and the temperature gradually increased to effect reaction and dehydration. During the latter part of the dehydration operation, 75 pounds of additional naphthenic-type oil was added so that the mixture would not become stiff and difficult to agitate at any time. Approximately 3 hours was required to complete the dehydration and at the end of this time the material in the kettle exhibited a slight acidity. After the dehydration had been completed the kettle contents were heated to a temperature of 300° F. and maintained at this temperature for a period of two hours. The material was then cooled to 200° F., about one gallon of water added and thoroughly mixed in, and the temperature then increased to 280° F., to effect dehydration. Finally as the complex barium soap grease cooled from 280° F., an additional 100 pounds of naphthenic-type oil was graded into the batch and at a temperature of about 200° F., 1.4 pounds of phenyl-alpha-naphthylamine, an oxidation inhibitor, was mixed in, the grease further cooled to room temperature, worked in the cold, and drawn into packages.

The finished grease had the following properties:

Composition

Complex barium soap	per cent by weight--	1 28.0
Oxidation inhibitor-----	do-----	0.5
Mineral oil-----	per cent--	71
Water content-----		Trace
Free fatty acid and unsaponifiable material-----	per cent--	0.5

¹ 0.75 mol barium acetate per mol of normal barium tallow fatty acid soap.

Physical characteristics

A. S. T. M. penetration at 77° F-----	317
Dropping point, °F-----	380
Resistance to boiling water-----	Excellent, not affected
Appearance-----	Smooth, transparent, slightly fibrous

EXAMPLE II

A complex barium soap grease was prepared in a manner similar to that described in Example I, except that the naphthenic-type oil employed had a viscosity at 100° F. of 600 Saybolt Universal seconds and one mol of barium acetate was employed for each mol of barium tallow fatty acid soap. Further, the grease was slightly alkaline, so prior to the hydration-dehydration operations, 2 pounds of tallow fatty acids were added and when the dehydration was almost complete, 1.14 pounds of barium hydrate was added in order that the finished product would be substantially neutral. The properties of this grease were as follows:

Composition

Barium tallow fatty acid soap	per cent by weight--	1 30.8
Oxidation inhibitor-----	per cent--	0.5
Free base-----		Trace
Water content-----		Trace
Mineral oil-----	per cent by weight--	68.7

¹ 1 mol barium acetate per mol of normal barium tallow fatty acid soap.

Physical characteristics

A. S. T. M. penetration at 77° F-----	300
Dropping point, °F-----	375
Resistance to boiling water-----	Excellent, not affected
Appearance-----	Smooth, transparent, slightly fibrous

EXAMPLE III

To a steam jacketed grease kettle equipped with means for agitation, 3400 parts by weight of barium hydrate and 650 parts by weight of glacial acetic acid were charged and mixed to effect reaction. A solution of 3000 parts by weight of tallow fatty acids in 1500 parts by weight of a naphthenic-type oil (viscosity at 100° F.=600 Saybolt Universal seconds) was added and while continuing agitation the mixture was heated to effect reaction and dehydration. During the final stage of the dehydration, an additional 4500 parts by weight of the naphthenic-type oil was added.

The resultant mixture was alkaline so it was cooled to 200° F., 1000 parts by weight of water and 100 parts by weight of tallow fatty acids added and the kettle contents again heated to about 280° F. to effect reaction and dehydration. An additional 9000 parts by weight naphthenic-type oil was then added, the product cooled to room temperature, worked and drawn into packages.

The properties of this complex barium soap grease were as follows:

Composition

Barium tallow fatty acid soap	per cent by weight--	1 26.1
Mineral oil-----	do-----	73.9
Free fatty acid-----		Trace
Water content-----		Trace

¹ 1 mol barium acetate per mol of normal barium tallow fatty acid soap.

Physical characteristics

A. S. T. M. penetration at 77° F.-----	295
Dropping point, °F.-----	376
Resistance to boiling water-----	Excellent, not affected

EXAMPLE IV

The following ingredients were weighed into a kettle:

	Parts by weight
Prime tallow (saponification number=193) --	56
Glacial acetic acid -----	4
Barium hydrate -----	46
Naphthenic type oil (viscosity=600 Saybolt Universal seconds at 100° F.) -----	56

While agitating, the material in the kettle was heated to 390° F. to effect reaction and dehydration. Subsequently, an additional 168 parts by weight of naphthenic-type oil was added and the material again heated to 390° F. The contents of the kettle were then cooled to room temperature, and about one part by weight of water added. While continuing agitation the grease was again heated to effect partial dehydration, subsequently cooled and worked to give a smooth, translucent product having an A. S. T. M. penetration at 77° F. of 189 and a Ubbelohde dropping point of 295° F.

EXAMPLE V

A complex barium soap grease was prepared in a manner similar to that described in Example 4, except that an equivalent amount of propionic acid was used in place of glacial acetic acid. A smooth, translucent product having an A. S. T. M. penetration at 77° F. of 180 and a Ubbelohde dropping point of 300° F. was obtained.

EXAMPLE VI

A complex barium soap grease was prepared in a manner similar to that described in Example 3, except that only one-half as much glacial acetic acid was employed and the remaining free barium hydroxide was neutralized by passing carbon dioxide through the kettle contents.

The resultant grease contained a complex barium soap comprising normal barium soap in combination with both barium acetate and barium carbonate. This product had an A. S. T. M. penetration at 77° F. of 250, a Ubbelohde dropping point above 400° F., and showed excellent stability and resistance to the effects of boiling water.

EXAMPLE VII

A complex barium soap grease was prepared in a manner similar to that described in Example 2, except that oil soluble sulfonic acids, such as are desired as by-products in the preparation of petroleum white oils, were used in place of the tallow fatty acids. This grease was likewise a smooth, translucent product having a dropping point above 350° F. and resistant to the effects of boiling water.

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

I claim:

1. A lubricating composition comprising mineral oil and a barium soap complex, the latter being an association complex comprising a normal barium soap and a barium salt in which the ratio of equivalents of barium salt to equivalents of normal barium soap is between about 0.1 and

3, said composition being substantially free from readily titratable excess alkalinity.

2. A lubricating composition comprising mineral oil and a barium soap complex, the latter being an association complex comprising a normal barium soap and a barium salt in which the ratio of equivalents of barium salt to equivalents of normal barium soap is between about 0.2 and 2.0, said composition being substantially anhydrous and free from readily titratable excess alkalinity.

3. A lubricating composition according to claim 1, in which the ratio of equivalents of barium salt to normal barium soap is between about 0.2 and 2.

4. A lubricating composition according to claim 1, in which the barium salt is a barium salt of a mineral acid.

5. A lubricating composition according to claim 1, in which the barium salt is a barium salt of low molecular weight organic acid.

6. A lubricating composition according to claim 1, in which the barium salt is barium carbonate.

7. A lubricating composition according to claim 1, in which the barium salt is barium acetate.

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

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

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

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

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

13. A lubricating composition according to claim 1 prepared by reacting approximately equal chemical equivalents of a basically reacting barium compound and a saponifiable material containing high molecular weight organic acids in the presence of mineral oil to yield a normal barium soap, adding aqueous solution of a barium salt and then heating said mixture to vaporize water therefrom.

14. A lubricating composition according to claim 1 prepared by heating a saponifiable material containing high molecular weight organic acids, low molecular weight organic acids and a basically reacting barium compound in the presence of mineral oil to yield a product containing said barium soap complex and then hydrating and dehydrating the product.

15. A lubricating composition according to claim 1 prepared by heating a low molecular weight organic acid, a basically reacting barium compound and a mineral oil containing high molecular weight organic acids to yield a product containing said barium soap complex, adding additional mineral oil and then hydrating and dehydrating said product.

16. A lubricating composition according to claim 1, in which the barium soap complex comprises a normal barium soap, a barium salt of a mineral acid and a barium salt of a low molecular weight organic acid.

17. A lubricating composition according to claim 1, in which the barium soap complex comprises a normal barium soap, barium carbonate and barium acetate.

18. A lubricating composition according to claim 1 containing also a small amount of an oxidation inhibitor.

19. A lubricating composition according to claim 1 containing also a small amount of phenyl alpha naphthylamine.

20. A method of preparing lubricants comprising reacting a saponifiable material, a basically reacting barium compound and low molecular weight organic acid in the presence of mineral oil to yield a product containing a barium soap complex and then adding additional mineral oil, said barium soap complex having a ratio of equivalents of barium salt of low molecular weight fatty acids to equivalents of barium soap of said saponifiable material between about

0.2 and 2.0 and being substantially free from readily titratable excess alkalinity.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
2,033,148	Ott et al.	Mar. 10, 1936
2,079,051	Sullivan et al.	May 4, 1937
2,154,383	Ott et al.	Apr. 11, 1939
2,197,263	Carmichael et al.	Apr. 16, 1940
2,283,581	Scalzitti	May 19, 1942
2,303,256	Camelford	Nov. 24, 1942
2,332,247	Morway et al.	Oct. 19, 1943
2,355,009	Morway et al.	Aug. 1, 1944

OTHER REFERENCES

McLennan, Methods of Compounding Barium Greases, Their Properties, Uses, and Future, Article in National Petroleum News, Apr. 5, 1944, pages R234, R236, R238, and R239.

Certificate of Correction

Patent No. 2,417,433.

March 18, 1947.

LESTER W. McLENNAN

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 1, line 36, for the word "desirable" read *derivable*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 8th day of July, A. D. 1947.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.

16. A lubricating composition according to claim 1, in which the barium soap complex comprises a normal barium soap, a barium salt of a mineral acid and a barium salt of a low molecular weight organic acid.

17. A lubricating composition according to claim 1, in which the barium soap complex comprises a normal barium soap, barium carbonate and barium acetate.

18. A lubricating composition according to claim 1 containing also a small amount of an oxidation inhibitor.

19. A lubricating composition according to claim 1 containing also a small amount of phenyl alpha naphthylamine.

20. A method of preparing lubricants comprising reacting a saponifiable material, a basically reacting barium compound and low molecular weight organic acid in the presence of mineral oil to yield a product containing a barium soap complex and then adding additional mineral oil, said barium soap complex having a ratio of equivalents of barium salt of low molecular weight fatty acids to equivalents of barium soap of said saponifiable material between about

0.2 and 2.0 and being substantially free from readily titratable excess alkalinity.

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