

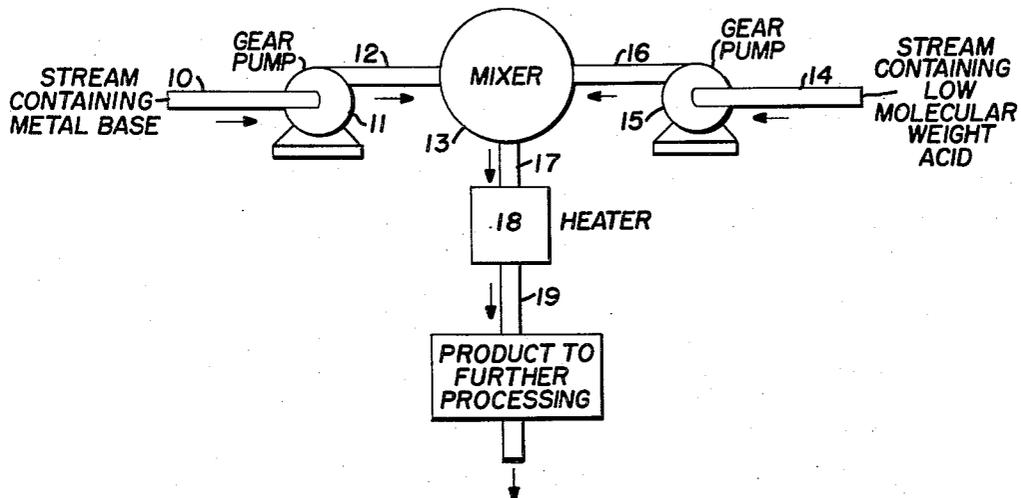
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PROCESS FOR PREPARING MIXED-SALT GREASE COMPOSITIONS

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## PROCESS FOR PREPARING MIXED-SALT GREASE COMPOSITIONS

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This invention relates to an improved method for preparing lubricating grease compositions thickened with a complex mixed-salt thickener and the compositions produced thereby. In particular, the invention relates to an improved process for preparing lubricating greases thickened with complex mixed-salt thickeners whereby a smooth, homogeneous and substantially grain-free (or grit-free) product is produced.

A complex mixed-salt thickener of the invention is formed by the neutralization with a metal base of (1) a low molecular weight organic and/or inorganic acid and (2) a high and/or intermediate molecular weight fatty acid. The complex mixed-salt thickener will therefore be formed from one of the following combination of acids:

(a) Low molecular weight acid and high molecular weight acid.

(b) Low molecular weight acid and an intermediate molecular weight acid.

(c) Low molecular weight acid, an intermediate weight acid and a high molecular weight acid.

In the preparation of these complex mixed-salt thickeners, the most generally used method of the prior art involved coneutralization of a mixture of acids. In the coneutralization method, a mixture of the low and high and/or intermediate molecular weight acids is neutralized with suitable bases, particularly the hydroxide and/or carbonate of the desired metals. This coneutralization step is generally carried out in a grease kettle "in situ," in the liquid menstium to which the complex compound is to be applied in actual use. For example, the mixed acids may be coneutralized in a portion or all of the lubricating oil forming the dispersant of a grease to be thickened by the mixed-salt complex. Coneutralization is possible in cases in which the salts have the same metal constituent, and the menstium is inert under the conditions of saponification or neutralization. The coneutralized material may be heated to temperatures of about 250° to 550° F. prior to use in order to dehydrate the product and to promote the formation of a complex in some instances, as when an alkaline earth metal hydrate is used.

The mixed-salt complex has also been prepared by separately performing at least a portion of the high and/or intermediate molecular weight carboxylic acid salt, intimately mixing this salt with the low molecular weight salt, and then heating, if necessary. This method is less desirable than coneutralization and is useful from a practical standpoint only when different metals are employed in forming the different salts.

It has also been known that when mixed-salt complexes are formed in a liquid dispersant or solvent, they may be isolated by solvent extraction of the dispersing medium in a solvent in which they are insoluble. Suitable solvents include hydrocarbons, alcohols, ketones, etc.; the proper choice depending on the solubility characteristics of the liquid menstium used to disperse the complex. However, this method is seldom used, as it is more desirable to form the complex thickener directly in the lubricating medium in which it is to be used, by the coneutralization method.

However, although the coneutralization method is the preferred method of forming complex mixed-salt thick-

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eners of the same metal, it has the disadvantage of forming a "gritty" (or grainy) grease (i. e., a grease which contains small, hard particles) when certain low molecular weight acids are used in forming the complex thickener. For example, in the formation of greases thickened with a complex mixed-salt thickener wherein the low molecular weight acid used in forming the complex is acetic acid and the metal base is hydrated lime, the formation of grit is particularly bad and very undesirable. This grit apparently results from the reaction of the low molecular weight acid with the metal base to form a salt which does not complex, i. e., enter into further reaction with the high and/or the intermediate molecular weight acid. It appears that these grits form around droplets of the low molecular weight acid which reacts with the metal base before these droplets are finally dispersed by the slow mixing of the grease kettle. This gritty substance once formed cannot be dispersed or eliminated by cooking, and milling or homogenizing merely reduces the size of the particles without removing them. Filtration can be used to remove the gritty particles; however, this is not favored as it results in a loss of material and is not practical in plant operations due to rapid plugging of the filter.

It has now been found that the amount and size of this grit is related to the degree of dispersion or of agitation during the addition of the low molecular weight acid to the mixture containing the metal base. This invention is therefore directed towards an improved process of preparing these complex mixed-salt thickeners which eliminates or at least substantially reduces the formation of objectionable grit particles.

The high molecular weight carboxylic acids contemplated in this invention are the saturated and unsaturated grease-making fatty acids that are commonly known in the art. In general, these fatty acids have from about 12 to 30 carbon atoms, preferably about 12 to 22 carbon atoms per molecule, having saponification values of from about 300 to 150. Suitable fatty acids include lauric, myristic acid, palmitic acid, stearic acid, the various hydroxy stearic acids, oleic acid, arachidic acid, behenic acid and the like. Naturally occurring fatty acids such as fish oil acids, tallow acid, coconut oil acids, etc. may also be utilized directly or after hydrogenation to decrease any undesirably high degree of unsaturation. Mixtures of these high molecular weight fatty acids, e. g. hydrogenated fish oil acids with oleic acid, in any proportions, are also operable, as are fractions obtained by distillation, extraction or crystallization.

The intermediate molecular weight monocarboxylic acids are those straight-chain, saturated fatty acids having from about 7 to 10 carbon atoms. Operable intermediate molecular weight carboxylic acids are exemplified by:

	Mol. weight	Sap. No. (mgs. KOH/gm.)
Enanthic (heptanoic).....	130	431
Caprylic (octanoic).....	144	389
Pelargonic (nonanoic).....	158	354
Capric (decanoic).....	172	326

Caprylic and pelargonic acids are preferred. The intermediate molecular weight carboxylic acids of even carbon chain lengths are normally obtained by processing from naturally occurring materials such as coconut oils. Pelargonic acid is obtained as a by-product in the production of azelaic acid by the ozonolysis of oleic acid.

Suitable low molecular weight acids include saturated and unsaturated aliphatic monocarboxylic acids having about 1 to 6 carbon atoms, such as formic, acetic,

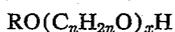
propionic, furoic, acrylic and similar acids including their hydroxy derivatives, such as lactic acid, etc. Saturated monocarboxylic acids having 1 to 3 carbon atoms per molecule are preferred. Formic and particularly acetic acid are especially preferred. Also, inorganic acids such as hydrochloric, phosphoric, nitric and/or sulfuric acids may be substituted for all or part of the low molecular weight organic acids.

Acetic acid, which is especially preferred, may be employed as glacial acetic acid or in a concentrated aqueous solution.

The metal components of the mixed-salts may be any group II metal, such as calcium, magnesium, barium or strontium, and may be supplied in the form of a metal base such as either the metal oxides, hydroxides or metal carbonates. Calcium hydroxide or hydrated lime is especially preferred.

The lubricating oil may be either a mineral base lubricating oil or various synthetic oils. Mineral base lubricating oils ranging in viscosity from about 30-1000 S. S. U.'s at 100° F. are preferably employed as the liquid phase of the grease compositions of the invention. These naturally occurring mineral lubricating oils may be derived from any petroleum crude source, whether paraffinic or naphthenic in type, and may be refined by any of the known refining techniques of the petroleum industry.

The invention is not limited, however, to the use of mineral base oils, since various synthetic oils having at least 30 Saybolt Universal viscosity at 100° F. may also be used as part or all of the liquid phase of the grease. Examples of operable synthetic lubricating oils include ether alcohols, such as those corresponding to the general formula



wherein R is an alkyl group, e. g. butyl,  $n$  is an integer from 2 to 5, and  $x$  is an integer from 1 to 40; esters of monobasic carboxylic acids, totalling 20 to 80 carbon atoms, such as those of  $C_4$  to  $C_{18}$  aliphatic acids with  $C_4$  to  $C_{18}$  aliphatic alcohols, the  $C_4$  to  $C_{18}$  radicals including the butyl, isobutyl, hexyl, octyl, iso-octyl, 2-ethyl hexyl, nonyl, decyl, lauryl, stearyl and similar radicals; diesters of dibasic acids, such as adipic or sebacic acid with monohydric alcohols, such as hexyl, octyl, 2-ethyl hexyl or higher alcohols; esters of polyethylene glycols with  $C_8$  to  $C_{18}$  branched-chain carboxylic acids; complex esters of polybasic carboxylic acids, polyhydric alcohols, and monobasic acids and/or monohydric alcohols, such as the glycol-centered or dibasic acid-centered complex esters; phosphoric acid esters or thioesters of aliphatic alcohols or mercaptans of up to about 18 carbon atoms; halocarbon oils, such as the polymers of chlorofluoro alkenes like chlorotrifluoroethylene; organo-siloxanes; sulfite esters, organic carbonates; mercaptans; formals, etc.

In preparing the lubricating grease composition of this invention, about 50 to 97 wt. percent of lubricating oil and from about 3 to 50 wt. percent of the complex thickener may be used. A preferred range is from about 10 to 30 wt. percent of the complex thickener, based on the weight of the total composition. This complex thickener, in turn, is prepared by using 1 mole of the high and/or intermediate molecular weight acid with about 3 to 15 mols, preferably 5 to 12 mols of the low molecular weight acid and about 2 to 8 mols, preferably 3 to 6 mols of the metal base.

Mixtures of the high and intermediate molecular weight acids may also be used in any ratios, e. g. about .15 to 50.0 mols of high molecular weight acid per mole of intermediate molecular weight acid.

The composition prepared in accordance with the invention may also contain various conventional additives, such as inhibitors, dyes, metal deactivators, corrosion preventives, deodorants, etc., as will be understood by those skilled in the art.

The improved process of the invention is carried out by achieving very intimate mixing of a stream which contains the low molecular weight acid with a stream containing the metal base. This process can be carried out in various ways. The stream which contains the low molecular weight acid may also contain part or all of the lubricating oil and the high and/or intermediate weight acids, or the lubricating oil and high and/or intermediate molecular acids may be part of the stream containing the metal base. The metal base may also be contained in the oil in one stream, while the other stream contains the low molecular weight acid and the high and/or intermediate molecular weight acid.

The essential condition is that one stream contains the low molecular weight acid while the other stream contains the metal base. However, since the low molecular weight acid will generally be insoluble in oil, it is preferred that the oil is not present in the stream containing the low molecular weight acid.

The preferred method of the invention employs a slurry stream of the oil menstuum, the metal base and the high and/or intermediate molecular weight acids as one stream. This slurry stream is fed concurrently with a stream of the low molecular weight acid into a mixing zone wherein the low molecular weight acid is very intimately dispersed into said slurry.

Examples of suitable mixers for achieving this intimate dispersion are described in "Manufacture and Application of Lubricating Greases," by C. J. Boner, published in 1954 by Reinhold Publishing Company, New York, N. Y., such as the Turbinizer (formerly called Lancaster Disperser) (pages 255-256), Charlotte Colloid Mill (pages 268-269), or simply a centrifugal pump. A homogenizer having a spring loaded valve, such as a Manton-Gaulin homogenizer, or other non-rotating mixers having high enough rates of shear may also be used. In short, any device will suffice that is capable of completing a mixing operation in less than five seconds and operating at a high enough rate of shear (5000 to 100,000 reciprocal seconds), to reduce the low molecular weight acid to drops of less than 0.05 mm. However, it is preferred to reduce the droplet size of the low molecular weight acid to 0.03 mm. or less.

The rate of shear for a rotary mixer is defined as:

$$Z = \frac{\pi D}{C} W$$

wherein,  $Z$ =rate of shear in reciprocal seconds,  $D$ =rotor diameter in inches,  $C$ =clearance in inches—rotor to case, and  $W$ =revolutions per second.

It is also necessary to apply a minimum of about 0.1 horsepower-second of energy to the mixer per pound of product to obtain the necessary degree of dispersion. The mixing zone therefore, should operate under a rate of shear of about 5,000 to 100,000 reciprocal seconds, e. g. 5,000 to 30,000 and an energy input of about .1 to 30, e. g. 5 to 15, horsepower-seconds of energy per pound of material introduced into said mixing zone.

The grease thus formed may then be dehydrated and heated to complex-forming temperatures by either conventional batch or by continuous methods.

The invention will be more fully understood by reference to the drawing and the following examples.

#### CONVENTIONAL CONEUTRALIZATION METHOD

A blend was prepared of the following ingredients:

	Percent by weight
Coastal mineral oil (pale) having a viscosity of 500 S. S. U. at 100° F., refined by conventional means	56.25
Hydrated lime—98.5 wt. percent $Ca(OH)_2$	11.25
Hydrogenated fish oil acids (10% $C_{14}$ , 25% $C_{16}$ , 45% $C_{18}$ , 10% $C_{20}$ , and 5% $C_{22}$ saturated acids)	3.75
Castor wax (hydrogenated castor oil)	3.75
60% aqueous acetic acid	25

The mixture of the above ingredients was heated in a conventional fire heated grease kettle to 450° F. in a period of 3 hours to dehydrate the product and to form the complex thickener.

METHOD OF PRESENT INVENTION

The present invention will be better understood by reference to the accompanying drawing. A slurry stream containing the metal base flows through line 10, to the intake of the gear pump 11, or other positive metering means. The slurry is then discharged from gear pump 11, at a constant rate through line 12, and enters the mixer 13. The stream containing the low molecular weight acid flows from a mixing or storage tank (not shown) through line 14, into the intake of the gear pump 15. The solution containing the low molecular weight acid is discharged from the gear pump 15, at a constant rate through line 16, into the mixer 13, where intimate mixing occurs between the slurry containing the metal base and the solution containing the low molecular weight acid. The resulting mixture is discharged from the mixer 13, through line 17, into the heater 18 where the mixture is dehydrated. The dehydrated mixture leaves the heater 18, through line 19, and is further processed to form the complex thickeners and the finished grease product.

Example I

A slurry was initially prepared by blending the following ingredients:

	Percent by weight
Coastal mineral oil (pale) having a viscosity of 500 S. S. U. at 100° F.....	75
Hydrated lime, 98.5 wt. percent Ca(OH) <sub>2</sub> .....	15
Castor wax (hydrogenated castor oil).....	5
Hydrogenated fish oil acids which is 10% C <sub>14</sub> , 25% C <sub>16</sub> , 45% C <sub>18</sub> , 10% C <sub>20</sub> , 5% C <sub>22</sub> saturated acids...	5

The slurry was heated to a temperature of 200° F. and maintained there sufficiently long to completely react the ingredients and was then cooled to 80° F. Referring to the drawing, the slurry was fed through line 10, to the gear pump 11, and was discharged from said pump 11, at the rate of 75 grams per minute through line 12, into the mixer 13, which was a 3" rotor diameter Gould centrifugal pump driven at 1750 R. P. M. by a ¼-horsepower motor. The mixer 13 provided a shear rate of about 10,000 reciprocal seconds rate of shear and an energy input of about 10 H. P. sec./lb. Concurrently, a 60% aqueous acetic acid solution was also fed through line 14, into the gear pump 15, from where it was discharged at the rate of 25 grams per minute into line 16, and into the mixer 13. The grease leaving the mixer 13, through its discharge line 17, was at a temperature of 144° to 150° F. and was well dispersed. This product was passed into the heater 18, where it was heated to a temperature of 300° F. over a period of time of about 50 sec. The discharge stream from the heater was then diluted with 1½ times its weight of additional mineral oil. Phenyl-alpha-naphthylamine at the rate of 0.5 wt. percent based on total weight of the composition, was added as an anti-oxidant. One portion (Example IA) was cooked for a period of about 1 hour and at a temperature of about 460° F. in a fire heated kettle equipped with agitators. The other portion (Example IB) was cooked in a continuous cooking apparatus where it was first passed through a heat exchanger and heated to a temperature of about 400° to 450° F., then passed through a heater where it was further heated to a temperature of about 500 to 510° F. to form the complex, followed by passing through a heat exchanger where it was cooled to about 225° to 275° F. and finally passed through a cooler where it was further cooled to a temperature of 150 to 250° F. The grease was then air cooled to room temperature.

The physical characteristics of the greases prepared

according to the above examples are shown in the following table.

TABLE 1

Method	Conventional	Present invention	
		Example IA	Example IB
Worked penetration at 60 strokes.	335 mm./10..	328 mm./10..	321 mm./10.
Dropping point, ° F.....	500°+.....	500°+.....	500°+.
ASTM wheel bearing test..	Pass.....	Pass.....	Pass.
Grit diameter (max.) (measured by microscope).	0.10 mm.....	0.02.....	0.02.

As seen from the above table, the complex thickened grease prepared in a conventional manner had grit particles having a maximum diameter of 0.10 mm. This grease showed roughness and had a very definite gritty feel when touched. The greases of Examples IA and IB of the invention, which were smooth and homogeneous in appearance, had a maximum grit diameter of 0.02 mm., and did not have a gritty feel, but were smooth and unctuous.

Example II

A slurry was prepared by blending the following ingredients:

	Percent by weight
Coastal mineral oil (pale) having a viscosity of 500 S. S. U.'s at 100° F.....	81.5
Hydrated lime 98.5 wt. percent Ca(OH) <sub>2</sub> .....	18.5

Referring to the drawing, the slurry was fed through line 10, to the gear pump 11, from where it was discharged through line 12, into the mixer 13 (which was the same Gould centrifugal pump described in Example I). Concurrently, an acid mixture of two parts by weight of glacial (99%) acetic acid and one part by weight of the light fraction distilled from coconut fatty acid, containing by weight 24.5% caprylic acid, 57.8% capric acid and 17.5% lauric acid, was fed through line 14, into the gear pump 15. The acid mixture was discharged from gear pump 15, through line 16, and into the mixer 13.

The pump ratio of the two gear pumps 11 and 15 was such as to give three parts by weight of slurry to one part of the mixed acids. The product discharged through line 17, from the mixer 13, was a heavy gel. This product passed through line 17, into the heater 18, where it was dehydrated by heating to a temperature of about 320° F. in about 25 seconds and then flashed to a vacuum dehydrator (Cornell homogenizer). Additional mineral oil was then added to the product in the amount of 38% by weight of mineral oil, based on the weight of the product from the mixer 13. The resulting mixture was then heated to about 500° F. in about 60 seconds to form the complex thickener. The resulting grease had the following characteristics:

TABLE 2

Worked penetration at 60 strokes.....	290 mm./10.
Dropping point.....	Over 500° F.
Timken OK load.....	43+ pounds.
Grit.....	None.

The above grease shown in Table 2 was smooth and homogeneous in appearance and completely grit-free.

What is claimed is:

1. A process for the manufacture of a lubricant comprising lubricating oil and about 3 to 50 weight percent of a mixed-salt complex comprising alkaline earth metal salt of a C<sub>1</sub> to C<sub>6</sub> fatty acid and alkaline earth metal salt of a higher molecular weight fatty acid selected from the group consisting of intermediate and high molecular weight fatty acids and mixtures thereof, which comprises forming a slurry containing alkaline earth metal base and at least a portion of the lubricating oil, passing a

stream of said slurry to a high intensity mixer, simultaneously passing to said mixer a second stream comprising said C<sub>1</sub> to C<sub>6</sub> fatty acid, one of said streams also containing said higher fatty acid, intensely mixing said streams in said mixer whereby said C<sub>1</sub> to C<sub>6</sub> fatty acid is dispersed in said slurry in the form of droplets of less than 0.05 mm. diameter, incorporating the remainder of said oil, heating to about 250 to 550° F. and cooling to form said lubricant.

2. A process according to claim 1, wherein said droplets are less than .03 mm. diameter.

3. A process according to claim 1, wherein said slurry also contains high molecular weight acid.

4. A process according to claim 1, wherein said slurry also contains intermediate molecular weight acid.

5. A process according to claim 1, wherein said metal base is selected from the group consisting of oxides, hydroxides and carbonates.

6. A process for the manufacture of a grit-free lubricating oil composition comprising lubricating oil and about 3 to 50 weight percent of a mixed-salt complex comprising an alkaline earth metal salt of a C<sub>1</sub> to C<sub>6</sub> fatty acid and an alkaline earth metal salt of a higher molecular weight fatty acid selected from the group consisting of high and intermediate molecular weight fatty acids and mixtures thereof, which comprises forming a slurry containing an alkaline earth metal base and at least a portion of the lubricating oil, introducing a stream of said slurry into a mixing zone functioning under a shear rate of about 5,000 to 100,000 reciprocal seconds and an energy input of about 0.1 to 30 horsepower seconds per pound of material introduced into said mixing zone, simultaneously introducing into said mixing zone a second stream comprising said C<sub>1</sub> to C<sub>6</sub> fatty acid, one of said streams also containing said higher molecular weight fatty acid, mixing said streams in said mixing zone, passing said mixed stream to a heating zone, incorporating the remainder of said oil, and heating to a temperature conducive to the formation of said mixed-salt complex and cooling to form said lubricant.

7. A process according to claim 6, wherein said shear rate is about 5,000 to 30,000 and wherein said energy input is about 5 to 15 horsepower seconds.

8. In a process for the manufacture of a lubricating grease comprising a mineral lubricating oil and a mixed-salt complex type grease thickener which in turn, comprises the calcium salt of acetic acid and the calcium salt of a mixture of hydrogenated castor oil and hydrogenated fish oil acids, wherein said complex grease thickener is formed in at least a portion of said mineral oil by the neutralization with lime of a mixture of hydrogenated castor oil, hydrogenated fish oil acids, and acetic acid, followed by heating said mixture to a temperature conducive to the formation of a complex to form a grease, and subsequently cooling said grease, the improvement which comprises highly dispersing said acetic acid in the form of droplets of about 0.02 mm. maximum diameter in a slurry comprising (a) lime, (b) hydrogenated castor oil, (c) hydrogenated fish oil acids and (d) mineral oil and then heating said dispersion to complex forming temperature and then cooling to form said grease.

9. In a process for the manufacture of lubricating grease comprising mineral lubricating oil and a mixed-salt complex type grease thickener which in turn comprises the calcium salts of acetic acid, caprylic acid, capric acid, and lauric acid, wherein said complex grease thickener is formed in at least a portion of said mineral oil by the neutralization with lime of a mixture of acetic, caprylic, capric, and lauric acids, followed by heating said mixture to a temperature conducive to the formation of a complex to form a grease and subsequently cooling said grease, the improvement which comprises, highly dispersing said mixture of acids in the form of droplets of less than about 0.02 mm. maximum diameter in a slurry of lime and mineral oil, followed by heating to form said mixed-salt complex and then cooling.

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