OVERBASED METAL CARBOXYLATE COMPLEX GREASE AND PROCESS FOR MAKING

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ABSTRACT

Complex greases of overbased alkaline earth metal carboxylates are prepared by reacting an overbased alkaline earth metal salt of a fatty acid, wherein the alkaline earth metal salt has an alkaline earth metal content of at least 14.5% and a non-volatile matter content of at least 95% with conversion agents to form a grease precursor. The grease precursor is then reacted with complexing agents to form a predominantly vaterite containing non-Newtonian modified overbased metal carboxylate complex grease.
OVERBASED METAL CARBOXYLATE COMPLEX GREASE AND PROCESS FOR MAKING

CROSS REFERENCE TO RELATED APPLICATION

[0001] The present application is being filed with the U.S. Receiving Office as a PCT application claiming priority from and any other benefit of U.S. provisional patent application Ser. No. 61/094,598 filed on Sep. 5, 2008, the entire disclosure of which is hereby incorporated by reference.

TECHNICAL FIELD

[0002] The invention relates to a complex grease prepared from an overbased alkaline earth metal soap of a fatty acid. More particularly, the invention relates to a vaterite grease prepared from an overbased metal carboxylate using one or more complexing agents during the manufacturing process.

BACKGROUND OF THE INVENTION

[0003] Making overbased alkaline earth metal soap greases includes either a one-step or two-step process. In a typical two-step process, the amorphous overbased alkaline metal soap which can be carboxylates, sulfonates, phenates or other organic acids based, or mixture of these, are first isolated, then these amorphous overbased alkaline metal soaps are converted to the crystalline form. The amorphous overbased alkaline metal soap normally is in the form of a micelle structure with an amorphous carbonate core dispersed in a hydrocarbon liquid of suitable viscosity. Such liquid grease precursor normally has a high TBN of 200-400 mg KOH/gm or even higher. While in a one-step process, the amorphous overbased alkaline metal soap is not separated, conversion from amorphous form to crystalline form is accomplished in-situ in the same reactor or some grease kettle in one step. Associated with this morphological change from amorphous form to crystalline form, the initial overbased material turns from a Newtonian liquid into a non-Newtonian gel or xanthic trope.

Unlike most of the neutral or near neutral metal soap thickened greases, either as simple metal soap greases or complex soap greases, the high TBN overbased metal soap thickened grease possesses many of the desirable performance features without the use of additives. Such performance features include good antiwear property, high load-carrying capability, high dropping point, excellent shear stability or mechanical strength, and many others depending on the nature of the overbased metal soap thickener and chemical process involved in grease manufacturing.

[0004] An important step in the production of any grease is the formation of the thickener microstructure. The microstructure of the crystalline material, or the matrix, in the grease enables the uptake and release of the lubricious oil. This is even more important for grease with overbased metal soap thickeners, since the thickener microstructure not only enables uptake and release of the lubricious oil, the thickener itself also acts as performance additives and provides many of performance attributes for the finished grease. The processing conditions such as temperature, pressure, residence times and saponification stoichiometry have tremendous influence on the thickener microstructure formed. The grease manufacturing process can also be characterized as one-stage or multi-stage process, such as conversion stage, complexing stage and finishing stage, based on the physical change and chemical reaction involved in grease making process. Therefore as a result, the process conditions and process stages will determine many of the performance attributes of the finished grease.

[0005] Thixotropic greases or grease-like overbased metal carboxylate or other overbased metal-containing compositions having acid neutralizing and detergency properties, and having utility for a variety of uses such as, for instance, in automobile and truck body undercoatings for rust inhibition, and for various other purposes, are known to the art. Such greases or grease-like compositions have gone into quite widespread use either as such, or admixed with other ingredients to produce compositions for use in a variety of environments, and, generally speaking, they are characterized by reasonably good extreme pressure and antiwear properties, high dropping points, reasonably good resistance to mechanical breakdown, salt spray and water-corrosion resistance, thermal stability at high temperatures, and other desirable properties.

[0006] Overbased metal carboxylates are generally produced by carbonating a mixture of hydrocarbons, carboxylic acid, metal oxide (calcium oxide for example) or metal hydroxide (calcium hydroxide for example) and promoters such as methanol and water. In carbonation, the calcium oxide or hydroxide reacts with the gaseous carbon dioxide to form calcium carbonate. The carboxylic acid is neutralized with an excess of CaO or Ca(OH)₂ to form the carboxylate. The prior art known processes for overbasing calcium carboxylates produce high alkaline materials having a TBN of 300 mg KOH/gm or higher. The TBN is the measurement of alkaline reserve, which is the number of milligrams of potassium hydroxide equivalent to the amount of acid required to neutralize the alkaline constituents present in one gram of sample. An additive having a total base number higher than that can be obtained from a stoichiometrically prepared calcium carboxylate alone is commonly termed “overbased” or, alternatively, is termed “superbasic”.

[0007] The addition of converting agents to overbased Newtonian solutions of calcium sulfonates or other overbased metal-containing materials along with heating and/or vigorous mixing, results in the formation of the non-Newtonian colloidal disperse systems. These converting agents include, among many others, water, alcohols, for instance, methanol, isobutanol, n-pentanol and many others or mixtures thereof or mixtures of alcohols with water; allyl eylene glycols; mono- and lower allylic ethers of allyl eylene glycols such as monomethyl ether of ethylene glycol; and numerous others such as lower aliphatic carboxylic acids exemplified by acetic acid and propionic acid; ketones; aldehydes; amines; phosphorus acids; alkyl and aromatic amines; certain imidazolines; alkanolamines; and, carbon dioxide as such, or better in combination with water. The resulting non-Newtonian colloidal disperse systems may be in the form of gels or greases depending upon the particular conditions, proportions and ingredients which are utilized in the preparation thereof.

[0008] In prior art overbased calcium-containing Newtonian solutions, the calcium carbonate which is formed during the preparation of the Newtonian solutions typically appears to be in an amorphous form whereas, when the Newtonian solutions are converted into the non-Newtonian colloidal disperse systems, the dissolved amorphous calcium carbonate salt or complex is typically transformed into solid crystalline particles of calcium carbonate, usually in the form of calcite, which then grow to form particle sizes which may range in
size from 40 to 50 angstroms (Å) or larger, for instance, up to 1000 Å or even up to 5000 Å. The calcium carbonate component of the overbased metal carbonate forms the core of a metal carbonate micellar structure.

In the case of an overbased alkaline earth metal carboxylate of a higher carboxylic acid such as oleic acid, the conversion agents such as water and acetic or propionic acid, when added to the Newtonian solution of amorphous calcium carbonate and calcium carboxylate, provides conversion of the amorphous calcium carbonate to vaterite, a spherical form of crystalline calcium carbonate, and none of the calciite is formed. This is in contrast to the overbased calcium sulfonates, which when treated with the conversion agents, form calcite or mixtures of calcite and vaterite micelles from the amorphous overbased calcium sulfonates.

Notwithstanding the state of the art as described herein, there is a need for further improvements in preparing predominantly vaterite containing greases modified with complex agents that have improved yield in terms of high oil incorporation and improved performance properties for shear stability, antiwear characteristics, extreme pressure or load carrying capability, dropping point and useful application temperature range.

SUMMARY OF THE INVENTION

In general, one aspect of the invention is to provide an overbased metal carboxylate complex grease. The overbased metal carboxylate complex grease includes an overbased alkaline earth metal salt of a fatty acid, wherein the alkaline earth metal salt has an alkaline earth metal content of at least 14.5% and a non-volatile matter content of at least 95%, conversion agents that include a hydrocarbon liquid, water, lime, a glycol, and a short chain carboxylic acid selected from the group consisting of acetic acid and propionic acid, and at least one complexing agent selected from the group consisting of phosphoric acid, boric acid, a C₁₂-C₂₄ aliphatic monocarboxylic acid and a C₁₂-C₂₄ fatty acid.

Another aspect of the invention is to provide a method for preparing a complex grease. The method includes the steps of:

- providing an overbased alkaline earth metal salt of a fatty acid, wherein the alkaline earth metal salt has an alkaline earth metal content of at least 14.5% and a non-volatile matter content of at least 95%;
- reacting the overbased alkaline earth metal salt of a fatty acid with conversion agents to form a Newtonian grease precursor, wherein the conversion agents comprise:
  - a hydrocarbon liquid;
  - water;
  - lime;
  - a polyol; and
  - a short chain carboxylic acid selected from the group consisting of acetic acid and propionic acid; and
- reacting the Newtonian grease precursor with at least one complexing agent to form a non-Newtonian complex grease, wherein the at least one complexing agent is selected from the group consisting of phosphoric acid, boric acid, a C₁₂-C₂₄ aliphatic monocarboxylic acid and a C₁₂-C₂₄ fatty acid.

DETAILED DESCRIPTION OF THE DRAWINGS

FIG. 1 is a representative X-Ray Diffraction spectrum of the vaterite form of calcium carbonate;
FIG. 2 is a representative X-Ray Diffraction spectrum of the calcite form of calcium carbonate;
FIG. 3 is a representative X-Ray Diffraction spectrum of an overbased calcium oleate carboxylate used in the preparation of the overbased calcium oleate complex grease;
FIG. 4 is a representative X-Ray Diffraction spectrum of an overbased calcium oleate complex grease according to one embodiment of the invention;
FIG. 5 are representative FTIR spectra of an overbased calcium sulfonate grease, an overbased calcium oleate carboxylate used in the preparation of the overbased calcium oleate complex grease, and an overbased calcium oleate complex grease according to one embodiment of the invention;
FIGS. 6a-6e are representative FTIR spectra of different overbased calcium oleate complex greases;
FIG. 7 is a representative FTIR spectra of an overbased calcium oleate carboxylate used in the preparation of the overbased calcium oleate complex grease and an overbased calcium oleate complex grease according to one embodiment of the invention;
FIGS. 8a-8d are representative FTIR spectra of commercially available overbased calcium sulfonate greases;
FIG. 9 is a representative FTIR spectra of a commercially available calcium sulfonate complex grease (A), calcium oleate complex grease (B), and Newtonian calcium oleate material (C); and
FIG. 10 is a representative FTIR spectra showing a change from amorphous to crystalline calcium carbonate during the formation of the calcium oleate complex grease.

DETAILED DESCRIPTION OF THE INVENTION

In a process for preparing a complex grease, a Newtonian overbased alkaline earth metal carboxylate, along with conversion agents that include water, lime, a hydrocarbon liquid, a glycol and a short chain carboxylic acid such as acetic acid and propionic acid, are reacted resulting in the formation of an intermediate, overbased grease precursor. The overbased grease precursor may then be combined, either alone or in combination, with complexing agents that include
phosphoric acid, boric acid and/or an aliphatic monocarboxylic or fatty acid such as a C_{12-24} acid. When reacted with conversion agents, the Newtonian overbased alkaline earth metal carboxylate is converted into a thixotropic, non-Newtonian gelled grease precursor predominantly containing vaterite. When combined with the complexing agents, the vaterite containing grease precursor is further modified to form an overbased complex grease having improved yield in terms of high oil incorporation and improved properties for mechanical shear resistance, extreme pressure, anti-wear and dropping point temperature.

In another process for preparing a complex grease, a Newtonian overbased alkaline earth metal carboxylate may react first with conversion agents then subsequently with complexing agents before the conversion from Newtonian overbased grease precursor to a non-Newtonian grease has completed. The conversion agents include water, lime, a hydrocarbon liquid, a glycol and a short chain carboxylic acid such as acetic acid and propionic acid. The complexing agents include phosphoric acid, boric acid and/or an aliphatic monocarboxylic or fatty acid such as a C_{12-24} acid. When reacted with both conversion and complexing agents, the Newtonian overbased alkaline earth metal carboxylate is converted into a non-Newtonian complex grease predominantly containing vaterite in one single stage reaction for production efficiency and process simplification. The vaterite containing complex grease formed through this one single stage reaction has improved properties for mechanical shear resistance, extreme pressure, anti-wear and dropping point temperature.

In one embodiment of the invention, the process for preparing the complex grease is a two-step process, the first step includes the process for manufacturing of a suitable Newtonian overbased metal soap solution and the second step includes a single stage reaction which converts the overbased metal soap solution from a Newtonian solution to a non-Newtonian grease. In this one stage reaction, the Newtonian overbased alkaline earth metal carboxylate and conversion agents are reacted for a predetermined amount of time such that the intermediate overbased grease precursor remains a Newtonian solution. Subsequent addition of the complexing agents converts the Newtonian intermediate overbased grease precursor to a non-Newtonian predominantly vaterite containing, modified overbased calcium carboxylate complex grease.

In another embodiment of the invention, the process for preparing the complex grease is a two-step process, wherein the first step includes the process for manufacturing of a suitable Newtonian overbased metal soap solution and the second step includes a two stage reaction. In this two-stage reaction, the first stage reaction includes reacting the Newtonian overbased alkaline earth metal carboxylate with the conversion agents for a predetermined amount of time such that the intermediate overbased grease precursor is a thickened, thixotropic non-Newtonian, gelled product. In the second stage of the reaction, the addition and reaction of the complexing agents with the grease precursor converts the thickened, non-Newtonian intermediate overbased grease precursor to a non-Newtonian predominantly vaterite containing, modified overbased calcium carboxylate complex grease.

The alkaline earth metal of the carboxylate is selected from the group consisting of calcium, barium, magnesium and strontium. These metals are derived from metal oxides and hydroxides, and in some instances, metal sulfides and hydrosulfides. For example, the grease precursor can include an overbased calcium carboxylate.

The carboxylic acid portion of the metal carboxylate, includes fatty acids, including C_{6-18} saturated, unsaturated carboxylic acids of 8 to 30 carbon atoms, either alone or in combination with each other, or reactive equivalents of carboxylic acids. Examples of useful carboxylic acids and fatty acids include but are not limited to caprylic acid, capric acid, lauric acid, myristic acid, myristoleic acid, 2-ethylhexanoic acid, decanoic acid, dodecanoic acid, pentadecanoic acid, palmitic acid, palmitoleic acid, stearic acid, 12-hydroxystearic acid, oleic acid, ricinoleic acid, linoleic acid, linolenic acid, arachidic acid, gadoleic acid, behenic acid, erucic acid, and mixtures of any of these acids.

The formation of the metal carboxylate may also include an alcohol that promotes the formation of the overbased alkaline earth metal carboxylate. The alcohol includes aliphatic alcohols that contain at least 8 carbon atoms. In one example, an aliphatic alcohol having 8 to 14 carbon atoms or more can be used. Examples of such aliphatic alcohols include isodecanol, dodecanol, octanol, tridecanol, tetradecanol or mixtures thereof. It has been found that when a higher aliphatic alcohol is employed in making the overbased product, phenol may be excluded from the reaction as a promoter.

The overbased metal carboxylate utilized in the making of the complex grease is prepared containing at least 12.5% by weight or more of the alkaline earth metal as calcium. In the preparation of higher metal-containing overbased products, for example, containing at least 15% by weight metal, it has been found suitable to use a polyl. The polyl can be a glycol or a glycol ether. The glycol or glycol ether may be selected from the group consisting of diethylene glycol monobutyl ether (butyl Carbitol®), triethylene glycol, dipropylene glycol, diethylene glycol monomethyl ether, ethylene glycol monobutyl ether, and mixtures thereof.

The process for preparing the overbased calcium carboxylate for use in the making of the complex grease includes reacting an alkaline earth metal base and a fatty acid with an equivalent ratio of metal base to the fatty acid being greater than 1:1 in the presence of at least one liquid hydrocarbon, an alcohol, and a polyl such as a glycol ether. The mixture may be acidified and carbonated to produce amorphous alkaline earth metal carbonate within the mixture. During carbonation, a dispersion may be added containing alkaline earth metal base, liquid hydrocarbon and an alcohol having at least 8 carbon atoms in relative amounts at a controlled rate of base addition to produce a stable liquid reaction product. During the reaction, water is removed from the reaction product to produce a shelf stable, flowable liquid overbased alkaline earth metal salt. Generally, the entire process may be conducted in the absence of free oxygen and, for this purpose, an atmosphere of nitrogen may be used.

By the term “acidic gas” as used in this specification and in the claims is meant a gas which upon reaction with water will produce an acid. Thus, such gases as sulfur dioxide, sulfur trioxide, carbon dioxide, carbon disulfide, hydrogen sulfide, etc., are exemplary of the acidic gases which are useful in the preparation of the overbased metal carboxylates disclosed. When carbon dioxide is used the alkaline earth carbonate is formed. When the sulfur gases are used, the sulfate, sulfide and sulfite salts are formed.

During carbonation of the overbased material, the mixture may be heated to a temperature which is sufficient to
drive off some of the water contained in the mixture or the water generated during the reaction of the base and the carboxylic acid can be retained during the overbasin reactions. The treatment of the mixture with the carbon dioxide preferably is conducted at elevated temperatures, and the range of temperatures used for this step may be any temperature above ambient temperature in the range from 75°C (167°F) to 200°C (392°F). Higher temperatures may be used such as 250°C (482°F), but there is no apparent advantage in the use of such higher temperatures. Ordinarily, a temperature of 80°C (176°F) to 150°C (302°F) is satisfactory.

[0051] After the removal of water from the alkaline earth metal base, fatty acid, polyol, liquid hydrocarbon and alcohol, the overbased material may be distilled or vacuum stripped at a temperature up to 165°C (330°F) to remove the volatile components of the reaction product. In distillation terminology, "striping" refers to the removal of a volatile component from a less volatile substance. The vacuum stripping proceeds until the final product has a measured alkaline earth metal content of at least 14.5% and a non-volatile matter content of at least 95%.

[0052] The overbased material used in the preparation of the complex grease is believed to be a thermodynamically stable microemulsion. The microemulsion has micelles and a continuous phase. The micelles consist of an alkaline earth metal carbonate and an alkaline earth metal carboxylate of the fatty acid. The continuous phase of the microemulsion consists of the liquid hydrocarbon and the alcohol.

[0053] Suitable conversion agents utilized in preparation of the overbased thixotropic, non-Newtonian gelled grease precursor include water; a hydrocarbon liquid including aliphatic hydrocarbons that are branched, straight chain or saturated cyclic structures, mineral spirits, non-aromatic hydrocarbons and polyalcohols (PAOs), Drakosol®, 600 is a suitable example of such hydrocarbon liquid; lime (Ca(OH)₂); alcohols, for instance, methanol, isobutanol, n-pentanol and many others or mixtures thereof or mixtures of alcohols with water; alkylene glycols; mono- and di-alkyl ethers of alkylene and propylene glycols such as monomethylether of ethylene glycol and propylene glycol; and numerous others such as lower aliphatic carboxylic acids including acetic acid and propionic acid.

[0054] Suitable complexing agents that may be added to the overbased, thixotropic non-Newtonian, gelled grease precursor to form a complex grease include water; phosphorus acids such as phosphoric acid; allyl and aromatic amines; boron acids, including boric acid, tetrahydrobromatic acid and metaphoric acid; and esters of such boron acids; and aliphatic or fatty acids of 12 to 24 carbon atoms which include dodecanoic acid, palmitic acid, stearic acid, oleic acid, ricinoleic acid, 12-hydroxy stearic acid. The hydroxy fatty acids, particularly hydroxy stearic acid, typically provide increased thickening to the grease when compared to unsubstituted fatty acids.

[0055] In one embodiment of the invention, a one-stage reaction for preparing the complex grease includes heating a Newtonian overbased calcium oleate material with conversion agents that include water, lime, a hydrocarbon solvent, propylene glycol and acetic acid under conditions favoring the formation of calcium carbonate crystals in the form of predominantly vaterite crystals, and not calcite, to form a Newtonian overbased grease precursor. The Newtonian overbased grease precursor is then combined with at least one of the complexing agents, the Newtonian grease precursor is subsequently converted into a predominantly vaterite containing thickened, non-Newtonian complex grease.

[0056] In another embodiment of the invention, a two-stage reaction for preparing the complex grease includes heating a Newtonian overbased calcium oleate material with conversion agents that include water, lime, a hydrocarbon solvent, propylene glycol and acetic acid under conditions favoring the formation of calcium carbonate crystals in the form of predominantly vaterite crystals, and not calcite, to form a thixotropic intermediate non-Newtonian, gelled grease precursor. The grease precursor is then combined with at least one complexing agent that includes water, phosphoric acid, boric acid and/or 12-hydroxy stearic acid. When combined with the complexing agents, the thixotropic intermediate non-Newtonian, gelled grease precursor is subsequently converted into a predominantly vaterite containing non-Newtonian complex grease.

[0057] The following Examples illustrate the components, as well as amounts, of the predominantly vaterite containing complex grease, but these examples are not considered to be limiting the scope of this invention.

EXAMPLES

Two-Step, One Stage Process for the Formation of Vaterite Containing Modified Overbased Calcium Oleate Complex Grease

Example 1

[0058] In a 3-gallon Hobart mixer was placed 1000.02 g of Drakesol® 600, 2000.14 g of 15.0% overbased calcium oleate (96.2% non-volatile matter (NVM) and 330 total base number (TBN), 100.09 g of lime (Ca(OH)₂), and the conversion agents including 200.06 g of water, 100.05 g of propylene glycol and 150.07 g of acetic acid. The mixture was heated with stirring to 104°C (220°F) for approximately one hour and thirty minutes to form an intermediate Newtonian grease precursor. Next, the complexing agents were added to the thickened, intermediate non-Newtonian grease precursor. The secondary conversion agents included 100.13 g of water, 149.99 g of 12-hydroxy stearic acid and 100.02 g of phosphoric acid. The mixture was heated with stirring at 104°C (220°F) for approximately one hour to form a predominantly vaterite containing non-Newtonian calcium 12-hydroxy stearate and calcium phosphate modified overbased calcium oleate complex grease. This complex grease may be considered a food grade complex grease.

[0059] The product was analyzed to contain no detectable calcite or aragonite by X-ray diffraction analysis.

Example 2

[0060] In a 3-gallon Hobart mixer was placed 1012.50 g of Drakesol® 600, 2000.00 g of 15.0% overbased calcium oleate (96.2% NVM and 330 TBN), 100.00 g of lime (Ca(OH)₂), and the conversion agents including 200.01 g of water, 100.00 g of propylene glycol and 150.07 g of acetic acid. The mixture was heated with stirring to 104°C (220°F) for approximately one hour and thirty minutes to form an intermediate Newtonian grease precursor. Next, the complexing agents were added to the intermediate Newtonian grease precursor. The complexing agents included 100.01 g of water, 150.0 g of 12-hydroxy stearic acid and 100.00 g of boric acid. The mix-
ture was heated with stirring at 104°C (220°F) for approximately one hour to form a predominantly vaterite containing non-Newtonian calcium 12-hydroxystearate and calcium borate modified overbased calcium oleate complex grease. Example 3

Example 6

Example 4

Example 7

Example 5

Example 8

Example 6

Example 7

Example 5

Example 8
nantely vaterite containing non-Newtonian calcium 12-hydroxysestearate modified overbased calcium oleate complex grease. This complex grease may be considered a food grade complex grease.

Example 9

In a 3-gallon Hobart mixer was placed 1000.02 g of Drakesol® 600, 2000.00 g of 15.0% overbased calcium oleate (96.2% NVM and 330 TBN), 49.99 g of lime (CaOH₂), and the conversion agents including 200.04 g of water, 100.12 g of propylene glycol and 175.04 g of acetic acid. The mixture was heated with stirring to 104° C. (220° F.) for approximately one hour and forty-five minutes to form an intermediate Newtonian grease precursor. Next, the complexing agents were added to the intermediate Newtonian grease precursor. The complexing agents included 100.02 g of water and 200.03 g of 12-hydroxysestearic acid. The mixture was heated with stirring in a temperature range from 138° C. (280° F.) for approximately two hours to form a predominantly vaterite containing non-Newtonian calcium 12-hydroxysestearate modified overbased calcium oleate complex grease. This complex grease may be considered a food grade complex grease.

Example 10

In a 3-gallon Hobart mixer was placed 1000.10 g of Drakesol® 600, 2000.00 g of 15.0% overbased calcium oleate (96.2% NVM and 330 TBN), 75.00 g of lime (CaOH₂), and the conversion agents including 200.00 g of water, 100.00 g of propylene glycol and 250.00 g of acetic acid. The mixture was heated with stirring to 104° C. (220° F.) for approximately one hour and ten minutes to form an intermediate Newtonian grease precursor. Next, the complexing agents were added to the intermediate Newtonian grease precursor. The complexing agents included 100.01 g of water and 200.10 g of 12-hydroxysestearic acid. The mixture was heated with stirring in a temperature range from 104° C. (220° F.) to 138° C. (280° F.) for approximately two hours and thirty minutes to form a predominantly vaterite containing non-Newtonian calcium 12-hydroxysestearate modified overbased calcium oleate complex grease. This complex grease may be considered a food grade complex grease.

Example 11

In a 3-gallon Hobart mixer was placed 1600.00 g of Drakesol® 600, 3200.00 g of 15.0% overbased calcium oleate (96.2% NVM and 330 TBN), 120.00 g of lime (CaOH₂), and the conversion agents including 320.00 g of water, 160.00 g of propylene glycol and 280.00 g of acetic acid. The mixture was heated with stirring to 104° C. (220° F.) for approximately one hour and thirty-five minutes to form an intermediate Newtonian grease precursor. Next, the complexing agents were added to the intermediate Newtonian grease precursor. The complexing agents included 160.02 g of water and 320.04 g of 12-hydroxysestearic acid. The mixture was heated with stirring in a temperature range from 104° C. (220° F.) to 138° C. (280° F.) for approximately one hour and forty-five minutes to form a predominantly vaterite containing non-Newtonian calcium 12-hydroxysestearate modified overbased calcium oleate complex grease. This complex grease may be considered a food grade complex grease.

Example 12

In a 3-gallon Hobart mixer was placed 1000.04 g of Drakesol® 600, 2000.06 g of 15.0% overbased calcium oleate (96.2% NVM and 330 TBN), 100.02 g of lime (CaOH₂), and the conversion agents including 200.03 g of water, 100.26 g of propylene glycol and 150.01 g of acetic acid. The mixture was heated with stirring to 104° C. (220° F.) for approximately two hours to form a thixotropic, intermediate non-Newtonian gelled grease precursor. Next, the complexing agents were added to the thixotropic, intermediate non-Newtonian gelled grease precursor. The secondary conversion agents included 100.03 g of water and 200.03 g of 12-hydroxysestearic acid. The mixture was heated with stirring in a temperature range from 104° C. (220° F.) to 138° C. (280° F.) for approximately one hour and twenty minutes to form a predominantly vaterite containing non-Newtonian calcium 12-hydroxysestearate modified overbased calcium oleate complex grease. This complex grease may be considered a food grade complex grease.

Example 13

In a 3-gallon Hobart mixer was placed 1600.25 g of Drakesol® 600, 3200.06 g of 15.0% overbased calcium oleate (96.2% NVM and 330 TBN), 160.00 g of lime (CaOH₂), and the conversion agents including 320.04 g of water, 160.00 g of propylene glycol and 240.00 g of acetic acid. The mixture was heated with stirring to 104° C. (220° F.) for approximately two hours to form a thixotropic, intermediate gelled non-Newtonian grease precursor. Next, the complexing agents were added to the thixotropic, intermediate non-Newtonian gelled grease precursor. The secondary conversion agents included 160.01 g of water and 320.11 g of 12-hydroxysestearic acid. The mixture was heated with stirring in a temperature range from 104° C. (220° F.) to 138° C. (280° F.) for approximately two hours to form a predominantly vaterite containing non-Newtonian calcium 12-hydroxysestearate modified overbased calcium oleate complex grease. This complex grease may be considered a food grade complex grease.

Example 14

In a 3-gallon Hobart mixer was placed 1000.33 g of Drakesol® 600, 2000.04 g of 15.0% overbased calcium oleate (96.2% NVM and 330 TBN), 50.04 g of lime (CaOH₂), and the conversion agents including 200.00 g of water, 100.03 g of propylene glycol and 150.02 g of acetic acid. The mixture was heated with stirring to 104° C. (220° F.) for approximately two hours and thirty minutes to form a thixotropic, intermediate non-Newtonian gelled grease precursor. Next,
the complexing agents were added to the thixotropic, intermediate non-Newtonian gelled grease precursor. The complexing agents included 100.01 g of water and 200.02 g of 12-hydroxystearic acid. The mixture was heated with stirring in a temperature range from 104°C (220°F) to 138°C (280°F) for approximately one hour and fifteen minutes to form a predominantly vaterite containing non-Newtonian calcium 12-hydroxystearate modified overbased calcium oleate complex grease. This complex grease may be considered a food grade complex grease.

[0085] The product was analyzed to contain no detectable calcite or aragonite by X-ray diffraction analysis.

Example 15

[0086] In a 3-gallon Hobart mixer was placed 1000.07 g of Delcosol® 600, 2000.03 g of 15.0% overbased calcium oleate (96.2% NVM and 330 TBN), 99.99 g of lime (Ca(OH)₂), and the conversion agents including 200.01 g of water, 100.02 g of propylene glycol and 122.03 g of acetic acid. The mixture was heated with stirring to 104°C (220°F) for approximately two hours to form a thixotropic, intermediate non-Newtonian gelled grease precursor. Next, the complexing agents were added to the thixotropic, intermediate non-Newtonian gelled grease precursor. The complexing agents included 100.00 g of water and 200.03 g of 12-hydroxystearic acid. The mixture was heated with stirring in a temperature range from 104°C (220°F) to 138°C (280°F) for approximately one hour and thirty minutes to form a predominantly vaterite containing non-Newtonian calcium 12-hydroxystearate modified overbased calcium oleate complex grease. This complex grease may be considered a food grade complex grease.

[0087] The product was analyzed to contain no detectable calcite or aragonite by X-ray diffraction analysis.

[0088] A distinguishing feature of the overbased calcium oleate complex greases, as prepared above, includes formation of calcium carbonate crystals in the form of predominantly vaterite crystals, and not calcite in the complex grease. As seen in FIGS. 1 and 2, X-Ray Diffraction (XRD) spectra are shown for vaterite and calcite respectively. For comparison purposes, FIG. 3 shows an XRD spectrum of a 15% overbased calcium oleate carboxylate used in the preparation of the overbased calcium oleate complex grease and FIG. 4 shows an XRD spectrum of the overbased calcium oleate complex grease. Based upon the XRD data of FIG. 3, it can be concluded that the 15% overbased calcium oleate carboxylate primarily contains amorphous calcium carbonate, with substantially limited, in any, detectable levels of calcium carbonate as calcite and/or vaterite. Furthermore, the XRD data for the overbased calcium oleate complex grease, as seen in FIG. 4, reveals that the vaterite is the predominant form of calcium carbonate present in the grease. It appears that the calcite form of calcium carbonate is not present in the grease.

[0089] Further evidence of the presence of the vaterite form of calcium carbonate present in the overbased calcium oleate complex grease is seen in FIG. 5. Fourier-Transform Infrared Spectroscopy (FTIR) spectra are presented for three different materials. The key feature in these spectra is the peak position within the 860-880 cm⁻¹ region. Peaks in this region correspond to a form of calcium carbonate. Typically, a peak within the region from 828-862 cm⁻¹ correspond to amorphous calcium carbonate; a peak within the range from 880-885 cm⁻¹ corresponds to the calcite form of calcium carbonate; and a peak within the range from 875-877 cm⁻¹ corresponds to the vaterite form of calcium carbonate. As seen in FIG. 5, the spectrum having a peak at 885.1 cm⁻¹ corresponds to a commercially available overbased calcium sulfonate grease that is shown to be predominantly the calcite form of calcium carbonate. The spectrum having a peak at 856.7 cm⁻¹ corresponds to a commercially available overbased calcium oleate carboxylate liquid that contains predominantly amorphous calcium carbonate. The spectrum with a peak at 875.9 cm⁻¹ corresponds to an overbased calcium oleate complex grease according to one embodiment of the invention that contains predominantly the vaterite form of calcium carbonate.

[0090] As seen in FIG. 7, additional FTIR spectra are shown comparing the measurements of an overbased calcium oleate carboxylate liquid used in the preparation of the overbased calcium oleate complex grease and the overbased calcium oleate complex grease. The spectrum having a peak at 858.6 cm⁻¹ corresponds to a commercially available overbased calcium oleate carboxylate liquid that contains predominantly amorphous calcium carbonate. The spectrum with a peak at 875.0 cm⁻¹ corresponds to an overbased calcium oleate complex grease according to one embodiment of the invention that contains predominantly the vaterite form of calcium carbonate.

[0091] As seen in FIGS. 8a-8d, further FTIR spectra are presented for commercially available overbased calcium sulfonate complex greases. In each of these figures, it can be seen that the peaks corresponding to calcium carbonate is within the range from 890.8 cm⁻¹ to 884.7 cm⁻¹ which falls within the range corresponding to the calcite form of calcium carbonate.

[0092] Infrared analysis was also used to monitor and characterize the complex grease conversion process. It is known that infrared absorbance peaks at about 863 cm⁻¹, 877 cm⁻¹ and 882 cm⁻¹ are characteristic of amorphous calcium carbonate, vaterite carbonate calcium and calcite calcium carbonate respectively. In FIG. 9, FTIR spectrum showed clearly that Newtonian overbased calcium oleate material has a representative broad peak centered at 860 cm⁻¹. Both peak position and broadness of the peak are evidence indicating the amorphous nature of the calcium carbonate contained in the overbased calcium oleate material. Once the overbased calcium oleate material is converted to the non-Newtonian calcium oleate complex grease, the FTIR spectrum showed that the broad peak at 860 cm⁻¹ disappeared and was replaced with a sharp new peak at 875 cm⁻¹. This is consistent with a conversion from the amorphous calcium carbonate to the vaterite form of crystalline calcium carbonate. As a comparison, FTIR spectrum for a commercially available food grade calcium sulfonate complex grease was also shown in FIG. 9. It showed a main peak at 885 cm⁻¹, indicating calcite form of crystalline calcium carbonate.

[0093] Infrared analysis was also used to record the preparation of the complex grease process from start to finish as shown in FIG. 10. These FTIR spectra were recorded every 20 minutes on samples taken from the grease kettle. The FTIR spectra showed only one broad peak at 860 cm⁻¹ from room temperature to 210°C, when the overbased calcium oleate material is in the form of a Newtonian liquid. At 220 to 225°C, which corresponds to the point that overbased calcium oleate material is being converted to a thixotropic, non-Newtonian gel grease precursor, but before the start of the complexing reaction, the FTIR spectrum showed two peaks both at 860 cm⁻¹ and 875 cm⁻¹. Once the grease kettle is heated beyond 225°C and the grease reaction is pushed into the final complexing reaction stage, FTIR spectra showed only one
peak at 875 cm$^{-1}$. During the entire heating process, no infrared absorption band at wave number higher than 875 cm$^{-1}$ can be observed. Therefore, it can be concluded from the infrared analysis that for the overbased calcium oleate material, when amorphous calcium carbonate is converted to grease, it converts exclusively to the vaterite form of calcium carbonate.

[0094] The overbased chemistry provides for grease formulations that can be registered as food grade, biodegradable and biobased. The overbased complex grease contains calcium oleate, promoters made from materials that include propylene glycol and conversion agents that include water, lime, 12-hydroxystearic acid, and acetic acid, all of which are listed under the NSF registry for incidental food contact. The hydrocarbon solvents used in the grease formulations can be either synthetic or non-synthetic. The gelled material can be adjusted to the NLGI grade by using a suitable oil to yield a H1 food grade grease. A vegetable derived formulation can be adjusted to meet an NLGI #2 grease by using natural soybean oil, for example, rendering the resulting grease biodegradable. The grease can be categorized as biobased and biodegradable when the grease is made from vegetable-derived oleic acid and a low oil content consisting of a vegetable-derived oil such as canola or palm oil.

[0095] Due to the fact that oleic acid is a natural, monounsaturated fatty acid, an optional antioxidant additive may be used to improve the oxidative resistance of the complex grease. In one embodiment, an amine antioxidant may be utilized in preparing the overbased complex grease. The amine antioxidant, for example, may be added in an amount of typically less than 1.0% by weight of the total complex grease formulation. In yet another example, the amine antioxidant may be added in an amount of about 0.5% by weight of the total complex grease formulation.

[0096] Some common grease performance tests were conducted on an experimental food grade version of calcium oleate complex grease with 3.5% 12-hydroxystearic acid as a complexing agent. This base grease formulation was optimized in terms of the ratio of overbased calcium oleate grease starting material to 12-hydroxystearic acid as the complexing agent. It has also been optimized in terms of the ratio of the additional calcium hydroxide to the total amount of acids added during grease cooking process. Except for data gathered on 500 hours Grease Oxidation Stability Test (ASTM D942), which is obtained on the same base grease fortified with 0.5% amine antioxidant, all the other test results were obtained on the base grease without any performance additives. The results of these selected grease performance tests are listed in Table 2. For comparison, the typical performance data on one food grade type (H1) of commercial calcium sulfonate complex grease are also listed in Table 2.

<table>
<thead>
<tr>
<th>TABLE 2-continued</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grease Test</td>
</tr>
<tr>
<td>NLGI Grade</td>
</tr>
<tr>
<td>Penetration 60 strokes, mm/10</td>
</tr>
<tr>
<td>Penetration 10k strokes, mm/10</td>
</tr>
<tr>
<td>Mechanical Stability</td>
</tr>
<tr>
<td>Roll Stability 2 hrs @ 77° F, %</td>
</tr>
<tr>
<td>Drop Point, + C. (F)</td>
</tr>
<tr>
<td>Water Washout @ 175° F, % lost</td>
</tr>
<tr>
<td>Timken OK Load, lb (LBS),</td>
</tr>
<tr>
<td>Four Ball Wear, mm</td>
</tr>
<tr>
<td>Four Ball EP</td>
</tr>
<tr>
<td>Load Wear Index</td>
</tr>
<tr>
<td>Weld, kg</td>
</tr>
<tr>
<td>Oxidation Stability 100 hours kPa (PSI)</td>
</tr>
<tr>
<td>Rust Inhibition/ Bearing Corrosion</td>
</tr>
<tr>
<td>Copper Corrosion</td>
</tr>
<tr>
<td>Wheel Bearing</td>
</tr>
<tr>
<td>Leakage, grams</td>
</tr>
<tr>
<td>Oil Separation, % Loss</td>
</tr>
<tr>
<td>Evaporation loss, %</td>
</tr>
<tr>
<td>Loss @50° C.</td>
</tr>
<tr>
<td>Grease Mobility, g/min. @-18° C.</td>
</tr>
<tr>
<td>Low Temperature Torque @-18° C.</td>
</tr>
<tr>
<td>Shart, g-cm</td>
</tr>
</tbody>
</table>

*Note: Food Grease amine antioxidant was used in an amount of 0.5% by weight.

[0097] Based upon the foregoing disclosure, it should now be apparent that the vaterite containing complex grease as described herein will carry the objects set forth hereinabove. It is, therefore, to be understood that any variations evident fall within the scope of the claimed invention and thus, the selection of specific component elements can be determined without departing from the spirit of the invention herein disclosed and described.

What is claimed is:

1. An overbased metal carboxylate complex grease comprising:
   an overbased alkaline earth metal salt of a fatty acid,
   wherein the alkaline earth metal salt has an alkaline earth metal content of at least 14.5% and a non-volatile matter content of at least 95%;
   conversion agents comprising:
   a hydrocarbon liquid;
   water;
   lime;
   a polyol; and
   a short chain carboxylic acid selected from the group consisting of acetic acid and propionic acid; and
   at least one complexing agent selected from the group consisting of phosphoric acid, boric acid, a C$_12$-C$_{24}$ aliphatic monocarboxylic acid and a C$_{12}$-C$_{24}$ fatty acid.
2. The complex grease of claim 1, wherein calcite is substantially not measurable in the grease.

3. The complex grease of claim 1, wherein vaterite is the predominant form of calcium carbonate present in the grease.

4. The complex grease of claim 1, wherein the fatty acid of the at least one complexing agent is 12-hydroxystearic acid.

5. The complex grease of claim 1, wherein the fatty acid of overbased alkaline earth metal salt is oleic acid.

6. The complex grease of claim 1, wherein an alkaline earth metal of the overbased alkaline earth metal salt is selected from the group consisting of calcium, barium, magnesium and strontium.

7. The complex grease of claim 1, wherein the overbased alkaline earth metal salt is calcium oleate.

8. The complex grease of claim 1, wherein the polyol is a glycol or a glycol ether selected from the group consisting of diethylene glycol monobutyl ether, triethylene glycol, dipropylene glycol, diethylene glycol monomethyl ether, ethylene glycol monobutyl ether, and mixtures thereof.

9. A method of preparing a complex grease, the method comprising the steps of:
   providing a overbased alkaline earth metal salt of a fatty acid, wherein the alkaline earth metal salt has an alkaline earth metal content of at least 14.5% and a non-volatile matter content of at least 95%;
   reacting the overbased alkaline earth metal salt of a fatty acid with conversion agents to form a Newtonian grease precursor, wherein the conversion agents comprise:
   a hydrocarbon liquid;
   water;
   lime;
   a polyol; and
   a short chain carboxylic acid selected from the group consisting of acetic acid and propionic acid; and
   reacting the Newtonian grease precursor with at least one complexing agent to form a non-Newtonian complex grease, wherein the at least one complexing agent is selected from the group consisting of phosphoric acid, boric acid, a C_{12}-C_{24} aliphatic monocarboxylic acid and a C_{12}-C_{24} fatty acid.

10. The method of claim 9, wherein calcite is substantially not measurable in the grease.

11. The method of claim 9, wherein vaterite is the predominant form of calcium carbonate present in the grease.

12. The method of claim 9, wherein the fatty acid of the at least one complexing agent is 12-hydroxystearic acid.

13. The method of claim 12, wherein the fatty acid of overbased alkaline earth metal salt is oleic acid.

14. The method of claim 9, wherein an alkaline earth metal of the overbased alkaline earth metal salt is selected from the group consisting of calcium, barium, magnesium and strontium.

15. The method of claim 9, wherein the overbased alkaline earth metal salt is calcium oleate.

16. A method of preparing a complex grease, the method comprising the steps of:
   providing a overbased alkaline earth metal salt of a fatty acid, wherein the alkaline earth metal salt has an alkaline earth metal content of at least 14.5% and a non-volatile matter content of at least 95%;
   reacting the overbased alkaline earth metal salt of a fatty acid with conversion agents to form a thixotropic, non-Newtonian gelled grease precursor, wherein the conversion agents comprise:
   a hydrocarbon liquid;
   water;
   lime;
   a polyol; and
   a short chain carboxylic acid selected from the group consisting of acetic acid and propionic acid; and
   reacting the non-Newtonian grease precursor with at least one complexing agent to form a non-Newtonian complex grease, wherein the at least one complexing agent is selected from the group consisting of phosphoric acid, boric acid, a C_{12}-C_{24} aliphatic monocarboxylic acid and a C_{12}-C_{24} fatty acid.

17. The method of claim 16, wherein calcite is substantially not measurable in the grease.

18. The method of claim 16, wherein vaterite is the predominant form of calcium carbonate present in the grease.

19. The method of claim 16, wherein the fatty acid of the at least one complexing agent is 12-hydroxystearic acid.

20. The method of claim 19, wherein the fatty acid of overbased alkaline earth metal salt is oleic acid.

21. The method of claim 16, wherein an alkaline earth metal of the overbased alkaline earth metal salt is selected from the group consisting of calcium, barium, magnesium and strontium.

22. The method of claim 16, wherein the overbased alkaline earth metal salt is calcium oleate.