A grease composition is disclosed, having from 50 to 99 weight percent of a lubricating base oil, from 1 to 30 weight percent of a thickener component including one or more of (i) one or more natural oil derivatives, (ii) one or more hydrogenated metathesized natural oils and/or natural oil derivatives, (iii) one or more amidated metathesized natural oils and/or natural oil derivatives, (iv) one or more, or two or more, carboxylic acids and/or derivatives thereof, and (v) one or more of a metal base compound, and from 1 to 15 weight percent of one or more optional additives. Processes for making grease compositions are also disclosed.
NATURAL OIL BASED GREASE COMPOSITIONS AND PROCESSES FOR MAKING SUCH COMPOSITIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] A claim of priority for this application under 35 U.S.C. §119(c) is hereby made to the following U.S. provisional patent application: U.S. Ser. No. 61/774,760 filed Mar. 8, 2013; and this application is incorporated herein by reference in its entirety.

BACKGROUND

[0002] A wide variety of greases have been developed over the years comprising a number of different formulations with a wide variation in associated properties. An important component found in greases is the thickening agent, which is often at least one metal soap, and differences in grease formulations have often involved this ingredient. Soap thickened greases constitute a significant segment by far of the commercially available greases worldwide. Simple soap greases, which are salts of long chain fatty acids and a neutralizing agent, are probably the most predominant type of grease in use today, with lithium 12-hydroxystearate being the thickener most often used. Complex soap greases, which generally comprise metal salts of a mixture of organic acids have also come into widespread use, particularly because of the various property advantages such type greases can possess (i.e. dropping points at least 20°F. higher than their corresponding simple soap greases).

[0003] We have found that the incorporation of hydrogenated metathesized natural oils and their derivatives as a thickener component in simple and complex greases provides for greases with reduced processing times and improved yields.

SUMMARY

[0004] In one aspect, a grease composition is disclosed. The grease composition comprises from 50 to 99 weight percent of a lubricating base oil, and from 1 to 30 weight percent of a thickener component. The thickener component comprises one or more of (i) one or more natural oil derivatives, (ii) one or more hydrogenated metathesized natural oils and/or natural oil derivatives, (iii) one or more ammidized metathesized natural oils and/or natural oil derivatives, (iv) one or more carboxylic acids and/or derivatives thereof, and (v) one or more of a metal base compound. In some embodiments, the one or more hydrogenated metathesized natural oils and/or natural oil derivatives comprises a hydrogenated metathesized soybean oil based wax. The grease composition may further comprise from 1 to 15 weight percent of one or more optional additives.

[0005] In another aspect, a process for preparing a simple grease composition is disclosed. The process comprises adding from 1 to 30 weight percent of a thickener component comprising one or more of (i) one or more natural oil derivatives, (ii) one or more hydrogenated metathesized natural oils and/or natural oil derivatives, (iii) one or more ammidized metathesized natural oils and/or natural oil derivatives, (iv) one or more carboxylic acids and/or derivatives thereof, to from 50 to 99 weight percent of a lubricating base oil, and charging this mixture to a kettle, mixer or equivalent vessel. This mixture is then heated to a temperature between about 140°F. to 200°F. for approximately 30-60 minutes, in order to dissolve the one or more carboxylic acids and/or derivatives thereof into the lubricating base oil. One or more of a metal base compound is then charged to this mixture in an amount slightly in excess of the stoichiometric amount required to neutralize the one or more carboxylic acids and/or derivatives thereof. The mixture is then maintained at a temperature between about 190°F. to about 270°F. for approximately 30-90 minutes to complete the neutralization and to effect a substantial dehydorination of the mixture. This mixture is then heated to about 350°F. to about 430°F. for up to approximately 60 minutes. Thereafter, the mixture is cooled with the assistance of incorporating an additional amount of the lubricating base oil and the removal of heat, to yield the grease composition. Optionally, from 1 to 15 weight percent of one or more additives may be added to the grease composition.

DETAILED DESCRIPTION

[0007] The present application relates to natural oil based grease compositions and processes for making such compositions.

[0008] As used herein, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. For example, reference to “a substituent” encompasses a single substituent as well as two or more substituents, and the like.

[0009] As used herein, the terms “for example,” “for instance,” “such as,” or “including” are meant to introduce examples that further clarify more general subject matter. Unless otherwise specified, these examples are provided only as an aid for understanding the applications illustrated in the present disclosure, and are not meant to be limiting in any fashion.
As used herein, the following terms have the following meanings unless expressly stated to the contrary. It is understood that any term in the singular may include its plural counterpart and vice versa.

As used herein, the term “natural oil” may refer to oil derived from plants or animal sources. The term “natural oil” includes natural oil derivatives, unless otherwise indicated. Examples of natural oils include, but are not limited to, vegetable oils, algae oils, animal fats, tall oils, derivatives of these oils, combinations of any of these oils, and the like. Representative non-limiting examples of vegetable oils include canola oil, rapeseed oil, coconut oil, corn oil, cottonseed oil, olive oil, palm oil, peanut oil, safflower oil, sesame oil, soybean oil, sunflower oil, linseed oil, palm kernel oil, tung oil, jatropha oil, mustard oil, camelina oil, penoyrcress oil, hemp oil, algal oil, and castor oil. Representative non-limiting examples of animal fats include lard, tallow, poultry fat, yellow grease, and fish oil. Tall oils are by-products of wood pulp manufacture. In certain embodiments, the natural oil may be refined, bleached, and/or deodorized. In some embodiments, the natural oil may be partially or fully hydrogenated. In some embodiments, the natural oil is present individually or as mixtures thereof.

As used herein, the term “natural oil derivatives” may refer to the compounds or mixture of compounds derived from the natural oil using any one or combination of methods known in the art. Such methods include metathesis, saponification, transesterification, esterification, interesterification, hydrogenation (partial or full), isomerization, amidation, oxidation, and reduction, individually or in combinations thereof. Representative non-limiting examples of natural oil derivatives include gums, phospholipids, waxes (e.g. non-limiting examples such as hydrogenated metathesized natural oil waxes and amidated hydrogenated metathesized natural oil waxes), soapstock, acidulated soapstock, distillate or distillate sludge, fatty acids and fatty acid alkyl ester (e.g. non-limiting examples such as 2-ethylhexyl ester), hydroxy substituted variations thereof of the natural oil. For example, the natural oil derivative may be a fatty acid methyl ester (“FAME”) derived from the glyceride of the natural oil. In some embodiments, a feedstock includes canola or soybean oil, as a non-limiting example, refined, bleached, and deodorized soybean oil (i.e., RBD soybean oil). Soybean oil typically comprises about 95% weight or greater (e.g., 99% weight or greater) triglycerides of fatty acids. Major fatty acids in the polyglycerol esters of soybean oil include saturated fatty acids, as a non-limiting example, palmitic acid (hexadecanoic acid) and stearic acid (octadecanoic acid), and unsaturated fatty acids, as a non-limiting example, oleic acid (9-octadecenoic acid), linoleic acid (9,12-octadecadienoic acid), and linolenic acid (9,12,15-octadecatrienoic acid). In one embodiment, one particular natural oil derivative is hydrogenated castor oil, which is the glyceride of 12-hydroxystearic acid. In some embodiments, hydrogenation and saponification of castor oil yields 12-hydroxystearic acid, which is then reacted with lithium hydroxide or lithium carbonate to give a high performance grease.

As used herein, the term “metathesis” or “metathesizing” refers to the reacting of a feedstock in the presence of a metathesis catalyst to form a metathesized product or “metathesized natural oil” comprising a new olefinic compound. Metathesizing may refer to cross-metathesis (a.k.a. co-metathesis), self-metathesis, ring-opening metathesis, ring-opening metathesis polymerizations (“ROMP”), ring-closing metathesis (“RCM”), and acyclic diene metathesis (“ADMET”). As a non-limiting example, metathesizing may refer to reacting two triglycerides present in a natural oil feedstock (self-metathesis) in the presence of a metathesis catalyst, wherein each triglyceride has an unsaturated carbon-carbon double bond, thereby forming a “natural oil oligomer” having a new mixture of olefins and esters that may comprise one or more of: metathesis monomers, metathesis dimers, metathesis trimers, metathesis tetramers, metathesis pentamers, and higher order metathesis oligomers (e.g., metathesis hexamers). Examples of metathesis compositions, processes, and products are reported in R. L. Pederson, Commercial Applications of Ruthenium Metathesis Processors; in “Handbook of Metathesis”, Vol. 2; R. H. Grubbs Ed.; Wiley-VCH Weinheim, Germany; 2003; pp. 491 to 510 (ISBN No. 3-527-30616-1). Of note, both intra- and inter-molecular cross-metathesis of unsaturated fatty acid glycerides in soybean oil results in long chain (e.g. C18 or higher) latent diacids.

As used herein, the term “metathesized natural oil” refers to the product formed from the metathesis reaction of a natural oil in the presence of a metathesis catalyst to form a mixture of olefins and esters comprising one or more of: metathesis monomers, metathesis dimers, metathesis trimers, metathesis tetramers, metathesis pentamers, and higher order metathesis oligomers (e.g., metathesis hexamers). In certain embodiments, the metathesized natural oil has been partially or fully hydrogenated, forming a “hydrogenated metathesized natural oil.” In certain embodiments, the metathesized natural oil is formed from the metathesis reaction of a natural oil comprising more than one source of natural oil (e.g., a mixture of soybean oil and palm oil). In other embodiments, the metathesized natural oil is formed from the metathesis reaction of a natural oil comprising a mixture of natural oils and natural oil derivatives.

As used herein, the term “dropping point,” “drop point,” or “melting point” are terms that may refer to the temperature at which the grease begins to melt. The drop point may be measured using ASTM-D127-08 or the Mettler Drop Point FP80 system, incorporated by reference herein.

As used herein, the term “needle penetration” may refer to the relative hardness of the grease composition. The needle penetration may be measured using ASTM-D1321-02a, incorporated by reference herein.

As used herein, the term “cone penetration” may refer to the measurement of the solidity of the grease. Penetration is the depth, in tenths of millimeters, to which a standard cone sinks into the grease under prescribed conditions. Thus higher penetration numbers indicate softer grease, since the cone has sunk deeper into the sample.

Grease Composition

The elements of a lubricating grease composition are generally divided among three parts: lubricating base oil, thickener, and additives. In general, the roles of these three parts is that the base oil carries out the main role of lubrication, the thickener structures the lubricating base oil into a semi-solid, and the additives impart additional functionality to the lubricating base oil and/or thickener, such as corrosion or oxidation resistance.

Lubricating Base Oil

The lubricating base oil employed in the grease composition can be any of the conventionally used lubricat-
ing oils, and is preferably a mineral oil, a synthetic oil or a blend of mineral and synthetic oils, or in some cases, natural oils and natural oil derivatives, all individually or in combinations thereof. Mineral lubricating oil base stocks used in preparing the greases can be any conventionally refined base stocks derived from paraffinic, naphthenic and mixed base crudes. The lubricating base oil may include polyolefin base stocks, of both polyalphaolefin (PAO) and polyinternal olefin (PIO) types. Oils of lubricating viscosity derived from coal or shale are also useful.

[0020] Examples of synthetic oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g., dodecylbenzenes, tetracyclicbenzenes, dinonylbenzenes, di(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof.

[0021] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, and etherification, constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having a number average molecular weight of 1000, diethylene ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500) or mono- and polyalkylarylated esters thereof, for example, the acetic acid esters, mixed C4-C15 fatty acid esters, or the C13 Oxo acid diester of tetraethylene glycol.

[0022] Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, linolenic acid dimer, malonic acid, malonic acids, and alkyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, and propylene glycol). Specific examples of these esters include dibutyl adipate, di-(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, diethyl phthalate, diecyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexyl monoester. Esters useful as synthetic oils also include those made from C6 to C12 monocarboxylic acids and polyols such as neopentyl glycol, trimethylol propane, and pentacerythritol, or polyol ethers such as dipentaerythritol, and tripropylene glycol.

[0023] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxy oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methylphenyl) silicate, tetra-(p-tert-butylphenyl)silicate, hexyl-(4-methyl-2-pentoxy)disiloxane, poly(methylsiloxanes) and poly-(methylphenyl)siloxanes). Other synthetic lubricating oils include liquid esters of phosphorous-containing acids (e.g., tricresyl phosphate, triethyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans.

[0024] Unrefined, refined and re-refined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used as lubricating base oil in the grease composition. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as re-refined or reprocessed oils and are often additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0025] Oils of lubricating viscosity can also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows:

<table>
<thead>
<tr>
<th>Category</th>
<th>Sulfur (%)</th>
<th>Saturates (%)</th>
<th>Viscosity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I</td>
<td>&gt;0.03</td>
<td>and/or &lt;90</td>
<td>80-120</td>
</tr>
<tr>
<td>Group II</td>
<td>=0.03</td>
<td>and ≥90</td>
<td>80-120</td>
</tr>
<tr>
<td>Group III</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Group IV</td>
<td></td>
<td>All polyalphaolefins (PAOs)</td>
<td></td>
</tr>
<tr>
<td>Group V</td>
<td></td>
<td>All others not included in Groups I, II, III, or IV</td>
<td></td>
</tr>
</tbody>
</table>

[0026] Groups I, II, and III are mineral oil base stocks. In some embodiments, the oil of lubricating viscosity is a Group I, II, III, IV, or V oil or mixtures thereof.

[0027] The lubricating base oil is present in a “major amount,” meaning greater than about 50 weight percent of the grease composition, preferably in the range 50 to 99 weight percent of the grease composition, preferably 60 to 95 weight percent of the grease composition, more preferably 70 to 92 weight percent of the grease composition and most preferably 75 to 90 weight percent of the grease composition. In general, these lubricating oils have a viscosity in the range of 15 to 220, preferably 30 to 150 cSt at 40°C, and a viscosity index in the range of 30 to 170, preferably 30 to 140.

Thickener

[0028] Another component in the subject grease composition is a thickener which serves to increase the consistency of the composition. The thickener generally comprises multiple components, which may include one or more of the following: (i) one or more natural oil derivatives, such as hydrogenated natural oils, (ii) one or more hydrogenated methylated natural oils and/or natural oil derivatives, (iii) one or more amidated methylated natural oils and/or natural oil derivatives, (iv) one or more carboxylic acids, such as 12-hydroxystearic acid (12-HSA) and azelaic acid, and derivatives
thereof, and (v) one or more of a metal base compound, such as metal oxide, metal hydroxide, or metal carbonate, or mixtures thereof.

[0029] The thickener may be present in a “minor amount,” meaning less than about 50 weight percent of the grease composition, preferably in the range of 1 to 30 weight percent of the grease composition, and more preferably 5 to 20 weight percent of the grease composition, and most preferably 10 to 20 weight percent of the grease composition. Generally, the function of the thickener is to provide a physical matrix which holds the lubricating base oil in a solid structure until operating conditions initiate viscoelastic flow.

A. Natural Oil Derivatives and Hydrogenated Metathesized Natural Oils

[0030] The natural oil derivatives may include one or more hydrogenated natural oils. Such hydrogenated natural oils may include: hydrogenated vegetable oil, hydrogenated algae oil, hydrogenated animal fat, hydrogenated tall oil, hydrogenated derivatives of these oils, and mixtures thereof. In one embodiment, the hydrogenated vegetable oil is hydrogenated canola oil, hydrogenated rapeseed oil, hydrogenated coconut oil, hydrogenated corn oil, hydrogenated cottonseed oil, hydrogenated olive oil, hydrogenated palm oil, hydrogenated peanut oil, hydrogenated safflower oil, hydrogenated soybean oil, hydrogenated sunflower oil, hydrogenated linseed oil, hydrogenated palm kernel oil, hydrogenated tung oil, hydrogenated jatropha oil, hydrogenated mustard oil, hydrogenated camelina oil, hydrogenated penayyris oil, hydrogenated castor oil, hydrogenated derivatives of these oils, and mixtures thereof. In another embodiment, the hydrogenated natural oil is a hydrogenated animal fat such as hydrogenated lard, hydrogenated tallow, hydrogenated poultry fat, hydrogenated fish oil, hydrogenated derivatives of these oils, and mixtures thereof. In some embodiments, the hydrogenated natural oil is hydrogenated castor oil.

[0031] In some embodiments, the thickener may have a component comprising a hydrogenated metathesized natural oil or a natural oil derivative thereof, such as a hydrogenated metathesized natural oil based wax. In many instances, the natural oil is metathesized and hydrogenated to modify the physical properties of the natural oil such that it forms a wax. Representative examples of hydrogenated metathesized natural oils include hydrogenated metathesized vegetable oil, hydrogenated metathesized algae oil, hydrogenated metathesized animal fat, hydrogenated metathesized tall oil, hydrogenated metathesized derivatives of these oils, and mixtures thereof. In one embodiment, the hydrogenated metathesized vegetable oil is hydrogenated metathesized canola oil, hydrogenated metathesized rapeseed oil, hydrogenated metathesized coconut oil, hydrogenated metathesized corn oil, hydrogenated metathesized cottonseed oil, hydrogenated metathesized olive oil, hydrogenated metathesized palm oil, hydrogenated metathesized peanut oil, hydrogenated metathesized safflower oil, hydrogenated metathesized sesame oil, hydrogenated metathesized soybean oil, hydrogenated metathesized sunflower oil, hydrogenated metathesized linseed oil, hydrogenated metathesized palm kernel oil, hydrogenated metathesized jatropha oil, hydrogenated metathesized mustard oil, hydrogenated metathesized camelina oil, hydrogenated metathesized pennycress oil, hydrogenated metathesized castor oil, hydrogenated metathesized derivatives of these oils, and mixtures thereof. In another embodiment, the hydrogenated metathesized natural oil is a hydrogenated metathesized animal fat such as hydrogenated metathesized lard, hydrogenated metathesized tallow, hydrogenated metathesized poultry fat, hydrogenated metathesized fish oil, hydrogenated metathesized derivatives of these oils, and mixtures thereof. In one embodiment, the natural oil is a hydrogenated metathesized soybean oil (“HMSBO”). In one embodiment, S-55 is a hydrogenated metathesized soybean oil available from Elevance Renewable Sciences, Woodridge, Ill. In one embodiment the HMSBO has a drop point of about 54°C (129°F), a congeal point of about 52°C (126°F) and a needle penetration of about 13 dmm. In another embodiment, the natural oil is a hydrogenated metathesized soybean oil that has been vacuum stripped to remove paraffins. In particular, this vacuum stripped version of HMSBO, S-60, is a hydrogenated metathesized soybean oil available from Elevance Renewable Sciences, Woodridge, Ill. In one embodiment, this vacuum stripped HMSBO has a drop point of about 54°C (129°F) and a needle penetration of about 1.9 dmm. For the purposes of this document, this vacuum stripped HMSBO shall also be included in the general definition of HMSBO.

[0032] Metathesis is a catalytic reaction generally known in the art that involves the interchange of allylicide units among compounds containing one or more double bonds (e.g., olefinic compounds) via the formation and cleavage of the carbon-carbon double bonds. Metathesis may occur between two like molecules (often referred to as self-metathesis) and/or it may occur between two different molecules (often referred to as cross-metathesis). Self-metathesis may be represented schematically as shown in Equation I.

\[
\begin{align*}
R^1 & \quad \text{CH} = \text{CH} & R^1 & \quad \text{CH} = \text{CH} & \qquad \text{II} \\
& \quad \text{CH} = \text{CH} & & \quad \text{CH} = \text{CH} & R^2 \\
& \leftrightarrow & R^1 & \quad \text{CH} = \text{CH} & R^2
\end{align*}
\]

[0033] wherein \( R^1 \) and \( R^2 \) are organic groups.

[0034] Cross-metathesis may be represented schematically as shown in Equation II.

\[
\begin{align*}
R^1 & \quad \text{CH} = \text{CH} & R^1 & \quad \text{CH} = \text{CH} & \qquad \text{II} \\
& \quad \text{CH} = \text{CH} & & \quad \text{CH} = \text{CH} & R^3 \\
& \leftrightarrow & R^1 & \quad \text{CH} = \text{CH} & R^3 \\
& & R^1 & \quad \text{CH} = \text{CH} & R^3 \\
& & & \quad \text{CH} = \text{CH} & R^1 \\
& & & \leftrightarrow & R^2 & \quad \text{CH} = \text{CH} & R^2 \\
& & & & \quad \text{CH} = \text{CH} & R^2
\end{align*}
\]

[0035] wherein \( R^1 \), \( R^2 \), \( R^3 \), and \( R^4 \) are organic groups.

[0036] In one embodiment, the hydrogenated metathesized natural oil based wax may be produced by the steps of: (a) providing a metathesis composition; (b) providing a metathesis catalyst comprising a transition metal; (c) metathesizing at least a portion of the metathesis composition in the presence of the metathesis catalyst to form a first composition comprising one or more metathesis products and transition metal; (d) hydrogenating at least a portion of the first composition in the presence of a hydrogenation catalyst to form a second composition comprising one or more hydrogenated metathesis products, transition metal, and hydrogenation catalyst; and (e) removing at least a portion of the hydrogenation catalyst from the second composition, wherein the removal of the hydrogenation catalyst removes at least a portion of the transition metal of the metathesis catalyst from the second composition.

[0037] In some embodiments, the metathesis compositions comprise polyol esters of unsaturated fatty acids. The polyol esters typically comprise one or more of monoacylglycerides, diacylglycerides, and triacylglycerides. The polyol esters are derived, for example, from natural oils. In one embodiment, the metathesis composition is refined, bleached, and deodor-
ized (i.e., RBD) soybean oil. The metathesis compositions may include esters of the fatty acids provided by the oils and fats and molecules with a single hydroxy site such as fatty acid methyl esters.

[0038] As used herein, “polyol esters” refers to esters produced from polyols. Polyols may include more than two hydroxyl groups. These polyols may comprise from two to about 10 carbon atoms, and may comprise from two to six hydroxyl groups, but other numbers of carbon atoms and/or hydroxyl groups are possible as well. The polyols may contain two to four hydroxyl moieties. Non-limiting examples of polyols include glyceral, 1,2-propanediol, 1,3-propanediol, 1,2-butandiol, 1,3-butandiol, 2,3-butandiol, 2-ethyl-1,3-propanediol, 2-ethyl-2-hydroxy-1,3-propanediol, neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol, trimethylolpropane (TMP), sorbitol and pentaerythritol. Very commonly, the polyol esters employed herein are esters of glyceral, e.g., triacylglycerides, or esters of a mixture of glyceral and one or more other polyols.

[0039] The polyol ester component may include a partial fatty acid ester of one or more polyols and/or a polyol which is fully esterified with fatty acids (“complete polyol fatty acid ester”). Examples of complete polyol fatty acid esters include triacylglycerides, propylene glycol diesters and tetra esters of pentaerythritol. Examples of suitable polyol partial esters include fatty acid monoglycerides, fatty acid diglycerides and sorbitan partial esters (e.g., diesters and triesters of sorbitan). In some embodiments, the polyol may include from 2 to 6 carbon atoms and 2 to 6 hydroxyl groups. Examples of suitable polyols include glyceral, trimethylolpropane, ethylene glycol, propylene glycol, pentaerythritol, sorbitan and sorbitol.

[0040] In some embodiments, the polyol esters are metathesized and hydrogenated to form wax compositions. For example, in one embodiment, refined, bleached and deodorized (RBD) soybean oil is self-metathesized in the presence of a metathesis catalyst to form a metathesis product. The resulting metathesis product is then hydrogenated without first removing the metathesis catalyst to form a hydrogenated metathesis product in the form of a wax. In some embodiments, the metathesis product is steam stripped and/or vacuum stripped in order to remove hydrocarbon impurities. For example, the metathesis product may be distilled in order to remove or reduce hydrocarbons having a molecular weight of about 200 gram/mole or less or to remove or reduce hydrocarbons having a molecular weight of about 300 grams/mole or less. The stripping may be accomplished by sparging the mixture in a vessel, typically agitated, by contacting the mixture with a gaseous stream in a column that may contain typical distillation packing (e.g., random or structured), or evaporating the light in an evaporator such as a wiped film evaporator. Typically, stripping will be conducted at reduced pressure and at temperatures ranging from about 100°C to 250°C. The temperature may depend, for example, on the level of vacuum used, with higher vacuum allowing for a lower temperature and allowing for a more efficient and complete separation of impurities. In one embodiment, the hydrogenated metathesized natural oil is a hydrogenated metathesized soybean oil that is vacuum stripped to remove paraffins. In particular, S-60 is a hydrogenated metathesized soybean oil available from Elevance Renewable Sciences, in Woodridge, Ill. In some embodiments, the hydrogenated metathesized natural oil and naturally occurring olefinic precursors may arise from bottoms streams from a metathesis reactor, or from bottoms streams of downstream separation units from a metathesis reactor. Such bottoms streams may be primarily esters, where such esters may include triglycerides, diglycerides, monoglycerides, or oligomers therefrom, or fatty acid methyl esters (“FAME”), or C10-C15 esters, C15-C18 esters, or C18 esters, or diesters therefrom, wherein such esters may occur as free esters or in combinations thereof. In some embodiments, such esters are preferably monoglycerides and/or fatty acid methyl esters.

[0041] The term “metathesis catalyst” includes any catalyst or catalyst system that catalyzes a metathesis reaction. Any known or future-developed metathesis catalyst may be used, individually or in combination with one or more additional catalysts. Non-limiting exemplary metathesis catalysts and process conditions are described in PCT/US2008/009635, pp. 18-47, incorporated by reference herein. A number of the metathesis catalysts as shown are manufactured by Materia, Inc. (Pasadena, Calif.). Additional exemplary metathesis catalysts include, without limitation, metal carbene complexes selected from the group consisting of molybdenum, osmium, chromium, rhodium, and tungsten. The term “complex” refers to a metal atom, such as a transition metal atom, with at least one ligand or complexing agent coordinated or bound thereto. Such a ligand typically is a Lewis base in metal carbene complexes useful for alkyne or alkene-metathesis. Typical examples of such ligands include phosphines, halides and stabilized carbenes. Some metathesis catalysts may employ plural metals or metal co-catalysts (e.g., a catalyst comprising a tungsten halide, a tetraalkyl tin compound, and an organoaluminum compound). An immobilized catalyst can be used for the metathesis process. An immobilized catalyst is a system comprising a catalyst and a support, the catalyst associated with the support. Exemplary associations between the catalyst and the support may occur by way of chemical bonds or weak interactions (e.g., hydrogen bonds, donor acceptor interactions) between the catalyst, or any portions thereof, and the support or any portions thereof. Support is intended to include any material suitable to support the catalyst. Typically, immobilized catalysts are solid phase catalysts that act on liquid or gas phase reactants and products. Exemplary supports are polymers, silica or alumina. Such an immobilized catalyst may be used in a fixed or fluid process. An immobilized catalyst can simplify purification of products and recovery of the catalyst so that recycling the catalyst may be more convenient.

[0042] The metathesis process can be conducted under any conditions adequate to produce the desired metathesis products. For example, stoichiometry, atmosphere, solvent, temperature and pressure can be selected to produce a desired product and to minimize undesirable byproducts. The metathesis process may be conducted under an inert atmosphere. Similarly, if the olefin reagent is supplied as a gas, an inert gaseous diluent can be used. The inert atmosphere or inert gaseous diluent typically is an inert gas, meaning that the gas does not interact with the metathesis catalyst to substantially impede catalysis. For example, particular inert gases are selected from the group consisting of helium, neon, argon, nitrogen and combinations thereof.

[0043] Similarly, if a solvent is used, the solvent chosen may be selected to be substantially inert with respect to the metathesis catalyst. For example, substantially inert solvents include, without limitation, aromatic hydrocarbons, such as benzene, toluene, xylene, etc.; halogenated aromatic hydrocarbons, such as chlorobenzene and dichlorobenzene; al-
phatic solvents, including pentane, hexane, heptane, cyclo-
hexane, etc.; and chlorinated alkanes, such as dichloromethane, chloroform, dichloroethane, etc.

In certain embodiments, a ligand may be added to the metathesis reaction mixture. In many embodiments using a ligand, the ligand is selected to be a molecule that stabilizes the catalyst, and may thus provide an increased turnover number for the catalyst. In some cases the ligand can alter reaction selectivity and product distribution. Examples of ligands that can be used include Lewis base ligands, such as, without limitation, trialkylphosphines, for example tricyclo-
heptylphosphine and tributyl phosphine; triarylphtophines, such as triphenylphosphate; dialkylalkylphosphines, such as, diphenylcyclohexylphosphine; pyridines, such as 2,6-dimethylypyridine, 2,6,4-trimethylpyridine; as well as other Lewis basic ligands, such as phospine oxides and phosphinites. Additives may also be present during metathesis that increase catalyst lifetime.

Any useful amount of the selected metathesis cata-
lst can be used in the process. For example, the molar ratio of the unsaturated polyl ester to catalyst may range from about 5:1 to about 10,000:1 or from about 50:1 to 500,000:1.

The metathesis reaction temperature may be a rate-
controlling variable where the temperature is selected to provide a desired product at an acceptable rate. The metathesis temperature may be greater than −40 °C, may be greater than about −20 °C, and is typically greater than about 0 °C or greater than about 20 °C. Typically, the metathesis reaction temperature is less than about 150 °C, typically less than about 120 °C. An exemplary temperature range for the metathesis reaction ranges from about 20 °C to about 120 °C.

The metathesis reaction can be run under any desired pressure. The total pressure may be selected to be greater than about 10 kPa, in some embodiments greater than about 30 kPa, or greater than about 100 kPa. Typically, the reaction pressure is no more than about 7000 kPa, in some embodiments no more than about 3000 kPa. An exemplary pressure range for the metathesis reaction is from about 100 kPa to about 3000 kPa.

In some embodiments, the metathesis reaction is catalyzed by a system containing both a transition and a non-transition metal component. The most active and largest number of catalyst systems are derived from Group VI A transition metals, for example, tungsten and molybdenum.

In some embodiments, the metathesis composition is thereafter hydrogenated with one or more hydrogenation catalysts. Such hydrogenation catalysts may comprise, for example, nickel, copper, palladium, platinum, molybdenum, iron, ruthenium, osmium, rhodium, or iridium. Combinations of metals may also be used. Useful catalysts may be heterogeneous or homogeneous. In some embodiments, the cata-
lysts are supported nickel or sponge nickel type catalysts.

In some embodiments, the hydrogenation catalyst comprises nickel that has been chemically reduced with hydrogen to an active state (i.e., reduced nickel) provided on a support. In some embodiments, the support comprises porous silica (e.g., kieselguhr, intestinal, diatomaceous, or siliceous earth) or alumina. The catalyst are characterized by a high nickel surface area per gram of nickel.

In some embodiments, the particles of supported nickel catalyst are dispersed in a protective medium comprising hardened triacylglyceride, edible oil, or tallow. In an exemplary embodiment, the supported nickel catalyst is dispersed in the protective medium at a level of about 22 wt. % nickel.

In some embodiments, the supported nickel cata-
lysts are of the type reported in U.S. Pat. No. 3,351,566 (Taylor et al.), incorporated herein by reference in its entirety. These catalyst comprise solid nickel-silica having a stabilized high nickel surface area of 45 to 60 sq. meters per gram and a total surface area of 225 to 300 sq. meters per gram. The catalysts are prepared by precipitating the nickel and silicate ions from solution such as nickel hydrosilicate onto porous silica particles in such proportions that the activated catalyst contains 25 to 50 wt. % nickel and a total silica content of 30 to 90 wt. %. The particles are activated by calcining in air at 600 to 900 °F, then reducing with hydrogen.

Useful catalysts having a high nickel content are described in EP 0 168 091, incorporated herein by reference in its entirety, wherein the catalyst is made by precipitation of a nickel compound. A soluble aluminum compound is added to the slurry of the precipitated nickel compound while the precipitate is maturing. After reduction of the resultant cata-
lyst precursor, the reduced catalyst typically has a nickel surface area of the order of 90 to 150 sq. m per gram of total nickel. The catalysts have a nickel/alumina atomic ratio in the range of 2 to 10 and have a total nickel content of more than about 66% by weight.

Useful high activity nickel/alumina/silica catalysts are described in EP 0 167 201, incorporated herein by reference in its entirety. The reduced catalysts have a high nickel surface area per gram of total nickel in the catalyst.

Useful nickel/silica hydrogenation catalysts are described in U.S. Pat. No. 6,846,772, incorporated herein by reference in its entirety. The catalysts are produced by heating a slurry of particulate silica (e.g. kieselguhr) in an aqueous nickel amine carbonate solution for a total period of at least 200 minutes at a pH above 7.5, followed by filtration, washing, drying, and optionally calcination. The nickel/silica hydrogenation catalysts are reported to have improved filtration properties.

Also useful are high surface area nickel/alumina hydrogenation catalysts, for example as reported in U.S. Pat. No. 4,490,480, incorporated herein by reference in its entirety. These catalysts typically have a total nickel content of 5 to 40% by weight.

Commercial examples of supported nickel hydrogenation catalysts include those available under the trade designations “NYSOFATC”, “NYSOSIL”, and “NI 5248 D” (from Engelhard Corporation, Iselin, N.J.). Additional supported nickel hydrogenation catalysts include those commercially available under the trade designations “PRICAT 9910”, “PRICAT 9920”, “PRICAT 9908”, “PRICAT 9936”, and “PRICAT 9925” (from Johnson Matthey Catalysts, Ward Hill, Mass.).

Hydrogenation may be carried out in a batch or in continuous process and may be partial hydrogenation or complete hydrogenation. In a representative batch process, a vacuum is pulled on the headspace of a stirred reaction vessel and the reaction vessel is charged with soybean oil (e.g., RBD soybean oil). The soybean oil may be heated to a desired temperature. Typically, the temperature ranges from about 50°C to 350°C, for example, about 100°C to 300°C or about 150°C to 250°C. The desired temperature may vary, for example, with hydrogen gas pressure. Typically, a higher gas pressure will require a lower temperature. In a separate
container, the hydrogenation catalyst is weighed into a mixing vessel and is slurried with a small amount of soybean oil. When the soybean oil reaches the desired temperature, the slurry of hydrogenation catalyst is added to the reaction vessel. Hydrogen gas is then pumped into the reaction vessel to achieve a desired pressure of H₂ gas. Typically, the H₂ gas pressure ranges from about 15 to 3000 psig, for example, about 40 to about 100 psig. As the gas pressure increases, more specialized high-pressure processing equipment may be required. Under these conditions the hydrogenation reaction begins and the temperature is allowed to increase to the desired hydrogenation temperature, where it is maintained by cooling the reaction mass, for example, with cooling coils. Typically, the hydrogenation temperature ranges from about 20°C to about 250°C, for example, about 100°C or greater, or about 120°C to about 220°C. When the desired degree of hydrogenation is reached, the reaction mass is cooled to the desired filtration temperature.

The amount of hydrogenation catalysts is typically selected in view of a number of factors including, for example, the type of hydrogenation catalyst used, the amount of hydrogenation catalyst used, the degree of unsaturation in the metathesis product, the desired rate of hydrogenation, the desired degree of hydrogenation (e.g., as measured by iodine value (IV)), the purity of the reagent, and the H₂ gas pressure. In some embodiments, the hydrogenation catalyst is used in an amount of about 10 wt. % or less, for example, about 5 wt. % or less or about 1 wt. % or less.

After hydrogenation, the used hydrogenation catalyst is removed from the hydrogenated metathesized product using known techniques such as filtration. In some embodiments, the hydrogenation catalyst is removed using a plate and frame filter such as those commercially available from Sparkle Filters, Inc., Connex Tex. In some embodiments, the filtration is performed with the assistance of pressure or a vacuum. In order to improve filtering performance, a filter aid may be used. A filter aid may be added to the metathesized product directly or it may be applied to the filter. Representative examples of filter aids include diatomaceous earth, silica, alumina, and carbon. Typically, the filtering aid is used in an amount of about 10 wt. % or less, for example, about 5 wt. % or less or about 1 wt. % or less. Other filtering techniques and filtering aids may also be employed to remove the used hydrogenation catalyst. In other embodiments the hydrogenation catalyst is removed using centrifugation followed by decantation of the product.

After filtering, the hydrogenated metathesis products typically contain less than about 100 ppm of the metathesis catalyst transition metal. In other embodiments, the hydrogenated metathesis products contain less than about 10 ppm of the metathesis catalyst transition metal. In still other embodiments, the hydrogenated metathesis products contain less than about 1 ppm of the metathesis catalyst transition metal, for example, about 0.9 ppm or less, about 0.8 ppm or less, about 0.7 ppm or less, about 0.6 ppm or less, about 0.5 ppm or less, about 0.4 ppm or less, about 0.3 ppm or less, or about 0.1 ppm or less. In exemplary embodiments, the metathesis catalyst is a ruthenium-based catalyst and the hydrogenated metathesis product contains less than about 0.1 ppm ruthenium.

In some embodiments, hydrogenated metathesized oil is a mixture of compounds of at least two general types: paraffinic compounds and triglycerides of long-chain monocarboxylic and di-carboxylic acids and oligomers thereof. The paraffinic compounds typically do not react under any fat splitting conditions and exit the reaction unaltered. Depending on the application, the paraffinic compounds can be partly or fully removed (stripped). Triglycerides and oligomers thereof are reacted with water or base to give mainly free fatty acids corresponding to the hydrogenated metathesized oil fatty acid profile (mono- and di-acids) and glycerol leaving small amounts of partially hydrolyzed hydrogenated metathesized oil composed of diglycerides, monoglycerides, and oligomers thereof.

In some embodiments, the metathesized natural oil may also be epoxidized. The metathesized natural oil may be epoxidized via any suitable peroxide acid. Peroxyacids (peracids) are acyl hydroperoxides and are most commonly produced by the acid-catalyzed esterification of hydrogen peroxide. Any peroxyacid may be used in the epoxidation reaction. Examples of hydroperoxides that may be used include, but are not limited to, peracetic acid, performic acid, m-dichloroperbenzoic acid, tert-butylhydroperoxide, triphenylsilylhydroperoxide, cumylhydroperoxide, and hydrogen peroxide.

B. Amided Metathesized Natural Oils

In some embodiments, the thickeners may have a component comprising an amidated hydrogenated metathesized natural oil or natural oil derivative, such as an amidated hydrogenated metathesized natural oil based wax. A number of valuable amide wax compositions may be prepared by reacting an amine with an ester-functional group of a metathesized natural oil in the presence of a basic catalyst or heat to form an amidated metathesized natural oil. This reaction may generate amidated metathesized natural oil compositions having unique properties over other forms of amide waxes, natural oils, or metathesized natural oils. Such unique properties may include a higher drop point, higher congeal point, improved hardness, improved malleability, improved emulsifiability, improved functionality, improved viscosity, and/or improved compatibility with other materials (such as triglyceride oils and waxes, polyamides, stearic acid, ethylene vinyl acetate copolymers, tackifier resins, and paraffins in low concentration). In certain embodiments, it is possible to tailor the range of certain properties (such as drop point or hardness) by modifying the amount or type of amine used in the reaction with the metathesized natural oil.

In certain embodiments, the metathesized natural oil in the amidated metathesized natural oil composition has been "hydrogenated" (i.e., full or partial hydrogenation of the unsaturated carbon-carbon bonds in the metathesized natural oil) in the presence of a hydrogenation catalyst to form a hydrogenated metathesized natural oil. In one embodiment, the natural oil is partially hydrogenated before it is subjected to the metathesis reaction. In another embodiment, the natural oil is metathesized prior to being subjected to partial or full hydrogenation. Any known or future-developed hydrogenation catalysts may be used, alone or in combination with one or more additional catalysts. Non-limiting exemplary hydrogenation catalysts were described previously in this document. Representative examples of hydrogenated metathesized natural oils were described previously in this document.

The amine compound(s) selected for the reaction with the metathesized natural oil may be ammonia or a compound containing one or more primary or secondary amino groups. In certain embodiments, the amine is a mono-substituted amine having one non-hydrogen substituted group
(such as an alkyl, aryl group, alkyl-amino group, or aryl-amino group), a di-substituted amine having two non-hydrogen substituted groups, an amino-alcohol, or a combination thereof. In certain non-limiting embodiments, the amine is a mono-substituted or di-substituted amine such as: methylamine, dimethylamine, ethylamine, diethylamine, propylamine, propylene, butylamine, dibutylamine, pentylamine, dipentylamine, hexylamine, dihexylamine, heptylamine, diheptylamine, octylamine, dioctylamine, or a mixture thereof. In other non-limiting embodiments, the amine is an amino-alcohol such as: methanolamine, dimethanolamine, diethanolamine, diisethanolamine, propyleneamine, dipropyleneamine, butanolamine, dibutanolamine, pentanolamine, dipentanolamine, hexanolamine, dihexanolamine, heptanolamine, diheptanolamine, octanolate, dioctanolate, aniline, or a mixture thereof. In yet other non-limiting embodiments, the amine is a diamine such as: ethylenediamine (1,2-ethanediamine), 1,3-propanediamine, 1,4-butanediamine (putrescine), 1,5-pentanediamine, 1,6-hexanedi, 1,7-heptanedi, 1,8-octanedi, 1,3-bis (aminomethyl)cyclohexane, meta-xylenediamine, 1,8-naphthalenediamine, p-phenylenediamine, N-(2-aminoethyl)-1,3-propanediamine, or a mixture thereof. In yet other non-limiting embodiments, the amine is a triamine or tetramine such as: diethylenetriamine, dipropylketetramine, dibutylketetramine, dipentylketetramine, dihexylenetriamine, diheptylenetriamine, dioctylenetetramine, spermidine, melamine, triethylenenetetramine, tripropylenetetramine, tributylenetetramine, tripentylenetetramine, tris(hexylenetetramine, triheptylenenetetramine, trioctylenenetetramine, hexamine, or a mixture thereof. In another embodiment, the amine is an imidazole or oxazolidine.

In one embodiment, the amine is selected from the group consisting of: ethanolamine, diethanolamine, diethylamine, 1,2-ethanedi, hexamethylenimine, and mixtures thereof. In one embodiment, the amine is ethylenediamine. In another embodiment, the amine is diethanolamine. In some embodiments, HMSBO may be fractionally amidated with diethanol amine to generate an emulsifying amidated wax, A100, available from Elevance Renewable Sciences, in Woodridge, Ill.

In certain embodiments, the amine is a polar compound that is useful for forming a hydrous amidated metathesized natural oil composition. The hydrous composition is capable of being water dispersible and improving the viscosity of the wax composition. Non-limiting examples of polar amines include amino-alcohols such as: methanolamine, dimethanolamine, ethanolamine, diethanolamine, propanolamine, dipropylanine, butanolamine, dibutanolamine, pentanolamine, dipentanolamine, hexanolamine, dihexanamine, heptanolamine, diheptanolamine, octanolamine, diocanamine, aniline, or mixtures thereof.

In other embodiments, the amine is a non-polar compound that is useful for forming an anhydrous amidated metathesized natural oil composition. Such anhydrous compositions may be capable of improving the hardness and drop point of the wax composition.

In one embodiment, the amount of amine present in the amine-metathesized natural oil reaction is between approximately 0.1 percent by weight and 30 percent by weight of the metathesized natural oil present. In other embodiments, the amount of basic catalyst is between approximately 0.1 percent by weight and 10 percent by weight of the metathesized natural oil or between approximately 1 percent by weight and 15 percent by weight of the metathesized natural oil. Alternatively, the amount of amine added to the reaction can be expressed in terms of the ratio of amine equivalents in the amine to ester equivalents in the metathesized natural oil. In one embodiment, the ratio of amine equivalents to ester equivalents is between approximately 1:100 and approximately 10:1. In another embodiment, the ratio of amine equivalents to ester equivalents is between approximately 1:10 and approximately 5:1. In other embodiments, the ratio of amine equivalents to ester equivalents is approximately 1:3, approximately 2:3, approximately 1:2, or approximately 1:1.

The basic catalyst that may be used to improve the reaction rate of the amine-metathesized natural oil reaction is a basic compound generally known to a person of skill in the art. In certain embodiments, the basic catalyst is sodium carbonate, lithium carbonate, sodium methanolate, potassium hydroxide, sodium hydride, potassium butoxide, potassium carbonate, or a mixture thereof. In certain embodiments, the basic catalyst may be added to the reaction between the amine and metathesized natural oil in dry form or dissolved in water.

In other embodiments, the reaction rate of the amine-metathesized natural oil reaction is improved by heating the amine-metathesized natural oil mixture (with or without a basic catalyst present) to at least 100°C, at least 120°C, at least 140°C, at least 160°C, or between approximately 100°C and approximately 200°C.

In one embodiment, the amount of basic catalyst added to the reaction is between approximately 1 percent by weight and 10 percent by weight of the metathesized natural oil present. In other embodiments, the amount of basic catalyst is between approximately 0.1 percent by weight and 1.0 percent by weight of the metathesized natural oil or between approximately 0.01 percent by weight and 0.1 percent by weight of the metathesized natural oil. In another embodiment, the amount of basic catalyst is approximately 0.5 percent by weight of the metathesized natural oil.

In one embodiment, the amine-metathesized natural oil reaction is conducted in a nitrogen or other inert atmosphere. In certain embodiments, the reaction is conducted under atmospheric conditions and the reactor temperature is between approximately 80-250°C, between approximately 120-180°C, or between approximately 120-160°C. In certain embodiments, the reactor temperature is held for approximately 1-24 hours, approximately 4-24 hours, approximately 1 hour, approximately 2 hours, approximately 4 hours, or approximately 6 hours.

In certain embodiments, following the amine-metathesized natural oil reaction, the product mixture is vacuum pumped for at least 30 minutes or at least 1 hour to separate the water, any unreacted amine, and/or glycerol from the amidated metathesized natural oil product. In another embodiment, paraffin byproduct from the metathesis and hydrogenation reactions can be separated from the amidated metathesized natural oil product.

In certain embodiments, when the metathesized natural oil is reacted with at least one amine in the presence of the basic catalyst or heat, the ester functionality is replaced by an amine to form an amidated metathesized natural oil comprising molecules having the following structures:
wherein \( R_1 \) is selected from the group consisting of:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{R} & \quad \text{O} \\
\text{R} & \quad \text{R} \\
\text{N} & \quad \text{N} \\
\text{R} & \quad \text{R} \\
\text{X}_1 & \quad \text{X}_2 \\
\end{align*}
\]

wherein \( R_2, R_3, R_4, R_5, R_6, R_7, R_8, \) and \( R_9 \) are independently selected from the group consisting of hydrogen, alcohols, aldehydes, propylene, and amine, wherein \( R_{10}, \) and \( R_{11} \) are independently selected from the group consisting of:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{R} & \quad \text{CH}_2 \\
\text{H} & \quad \text{O} \\
\text{H}_2 & \quad \text{O} \\
\end{align*}
\]

wherein \( R_{12} \) and \( R_{13} \) are independently selected from the group consisting of:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{X}_1 \\
\text{X}_2 & \quad \text{X}_3 \\
\text{X}_4 & \quad \text{X}_5 \\
\text{X}_6 & \quad \text{X}_7 \\
\end{align*}
\]

and \( X_1, X_2, X_3, X_4, X_5, \) and \( X_6 \) are independently selected from the group consisting of \( C_6-C_{28} \) saturated or unsaturated alkyl chains from either a fatty acid of a natural oil, or a derivative thereof formed by a metathesis reaction.

**C. Carboxylic Acids and Derivatives**

**[0082]** The carboxylic acid has about 2 to about 36, preferably about 6 to about 24, more preferably about 2 to about 20 carbon atoms, and mono-, di-, tri-, or poly-acid variants, hydroxy-substituted variants, aliphatic, cyclic, aliphatic, aromatic, branched, aliphatic- and allicylic-coated substituted aromatic, aromatic substituted aliphatic and allicylic groups, saturated and unsaturated variants, and heteroatom substituted variants thereof. In some embodiments, the mono- or di-esters or poly-esters of these acids thereof may be used. Non-limiting examples of such carboxylic acids include lauric acid, azelaic acid, myristic acid, palmitic acid, arachidic acid, behenic acid, lignoceric acid, oleic acid, linoleic acid, linolenic acid, capric acid, linolenic acid, decenoic acid, undecenoic acid, dodecenoic acid, ricinoleic acid, myristoleic acid, palmitoleic acid, gadoleic acid, elaidic acid, cis-9-eicosenoic acid, erucic acid, nervonic acid, 2,4-hexadecadienoic acid, linoleic acid, 12-hydroxytetradecaenoic acid, 10-hydroxytetradecaenoic acid, 12-hydroxyhexadecenoic acid, 8-hydroxhexadecenoic acid, 12-hydroxyicosanoic acid, 16-hydroxyicosanoic acid 11,14-eicosadienoic acid, linolenic acid, cis-8,11,14-eicosatrienoic acid, arachidonic acid, cis-5,8,11,14,17-eicospentanoic acid, cis-4,7,10,13,16,19-docosahexaenoic acid, all-trans-retinoic acid, lauric acid, oleic acid, stearic acid, linoleic acid, elaidic acid, linolenic acid, nervonic acid, abietic acid, absic acid, octadecenoic acid, nonadecenoic acid (azelaic acid), decanedioc acid (sebacic acid), undecanedioc acid, dodecanedioc acid, tridecanedioc acid, tetradecanedioc acid, pentadecanedioc acid and mixtures thereof. In some embodiments, azelaic acid is a preferred carboxylic acid. In some embodiments, naphthenic acids and mixtures thereof, such as are obtainable from various petroleum sources, may be used. Other non-limiting examples, such as the hydroxystearic, hydroxy-ricinoleic, hydroxybehenic and hydroxypalmatic acids may be used, preferably hydroxystearic acid or esters of these acids such as 9-hydroxy-, 10-hydroxy- or 12-hydroxy-stearic acid, and most preferably 12-hydroxy-stearic acid.
D. Metal Base Compound

[0083] In the metal base compound, the metals themselves can be selected from alkali metals or alkaline earth metals, such as, without limitation, beryllium, magnesium, calcium, lithium, sodium, potassium, strontium and barium; transition metals, without limitation, such as titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, zirconium, molybdenum, palladium, silver, cadmium, tungsten and mercury; and other metals such as aluminum, gallium, tin, iron, lead, and lanthanoid metals, all individually or in combinations thereof. Said metals are more preferably selected from lithium, sodium, magnesium, calcium, tin and barium. Examples of carboxylic acid metal salts which may be conveniently used in the present invention are metal salts of any combination of a mono- or poly-carboxylic; branched aliphatic, cyclic, cycloalkyl, or linear, saturated or unsaturated, mono- or poly-hydroxy substituted or unsubstituted carboxylic acid, acid chloride or the ester of said carboxylic acid with an alcohol such as an alcohol of about 1 to about 5 carbon atoms. As for the base compound, the alkoxydes, oxides, hydroxides, carbonates, chlorides, and mixtures thereof of any of the aforementioned metals are found to be especially useful. In some embodiments, hydroxides of these aforementioned metals are preferred, and calcium hydroxide, strontium hydroxide, magnesium hydroxide, sodium hydroxide, and lithium hydroxide are more preferred. The metal hydroxide is a mono- or di- or tri-valent metal or a mixture thereof. In one embodiment the metal hydroxide is lithium hydroxide monohydrate and can be solid or aqueous, although aqueous is preferred.

[0084] In some embodiments, the metal base, usually a metal hydroxide, such as lithium hydroxide or in its more commonly available form of lithium hydroxide monohydrate, is reacted with a carboxylic acid, usually 12-hydroxystearic acid, or with a carboxylic acid derivative, usually 12-hydroxy stearate or hydrogenated castor oil, to form a metallic (lithium) soap. This reaction is most often carried out in the lubricating base oil with water also being present. The water is added to act as a reaction solvent if the acid is used. If the carboxylic acid derivative is used, the water acts both as reaction solvent and reactant, the latter effect being necessary for the hydrolytic cleavage of the ester linkages in the 12-hydroxy stearate or the hydrogenated castor oil. In some embodiments, the lithium hydroxide is reacted with two or more carboxylic acids, such as 12-hydroxystearic acid and azelaic acid, to form a metallic (lithium) soap.

Optional Grease Additives

[0085] Various optional additives may be incorporated into the grease compositions of this invention, for the particular service intended. Such optional additives that may commonly be used include: metal deactivators, antioxidants, antitrust agents, rust inhibitors, viscosity modifiers, extreme pressure agents, corrosion inhibitors, and other additives recognized in the art to perform a particular function or functions. Such additives may be present in the range of 1 to 15 weight percent of the grease composition, and more preferably to 10 weight percent of the grease composition.

[0086] Metal deactivators may include derivatives of boronazoles, benzimidazoles, 2-alkylldithio-benz-imidazoles, 2-alkylldithio-benzthiazoles, 2-(N,N-dialkyl-dithiocarbamoyl)-benzothiazoles, 2.5-bis(alkyl-dithio)-1,3,4-thiadiazoles, 2.5-bis(N,N-dialkyl-dithiocarbamoyl)-1,3,4-thiadiaz oles, 2-alkylldithio-5-mercapto thiadiazoles or mixtures thereof. Antioxidants may include a variety of chemical types including phenate sulfides, phosphosulfurized terpenes, sulfurized esters, aromatic amines, and hindered phenols. Antiwear agents may include a metal thiophosphate, especially a zinc dialkyl dithiophosphate; a phosphoric acid ester or salt thereof; a phosphite; and a phosphorus-containing carboxylic ester, ether, or amide. Rust inhibitors may include metal sul fonates such as calcium sulfonate or magnesium sulfonate, amine salts of carboxylic acids such as octylamine octanoate; condensation products of dodecyl mercaptan acid or anhydride and a fatty acid such as oleic acid with a polyamine, e.g. a polyalkylene polyamine such as triethylenetetramine, and half esters of alkaryl mercaptan acids in which the alkaryl radical contains 8 to 24 carbon atoms with alcohols such as polyglycols.

[0087] Viscosity modifiers may include polymeric materials including styrene-butadiene rubbers, ethylene-propylene copolymers, polyisobutene, hydrogenated styrene-isoprene polymers, hydrogenated radical isoprene polymers, polymethacrylate acid esters, polyacrylate acid esters, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins, polyalkylenemethacrylates, esters of maleic anhydride-styrene copolymers and mixtures thereof. Extreme Pressure (EP) Agents may include agents that are soluble in the oil include a sulfur or chlorosulfur EP agent, a chlorinated hydrocarbon EP agent, or a phosphorus EP agent, or mixtures thereof. Examples of such EP agents are chlorinated wax, organic sulfides and polysulfides, such as benzyl disulfide, bis-(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized sperm oil, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons, such as the reaction product of phosphorus sulfide with turpentine or methyl oleate, phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphates, i.e., dibutyl phosphate, diheptyl phosphate, dicyclhexyl phosphate, pentylphenyl phosphate; dipentylphenyl phosphate, tridecyl phosphate, distearyl phosphate and polypropylene substituted phenol phosphate; metal thiocarbamates, such as zinc diocylthiocarbamate and barium heptylphenyl diacath, such as zinc dicyclohexyl phosphorodithioate and the zinc salts of a phosphorodithioic acid combination may be used. Corrosion inhibitors may include: mercaptobenzthiazole, barium diononylnaphthalene sulfonate, glycerol monooleate, sodium nitrite, and imidazolines of tetraethylene pentamine, among others.

Uses/Applications for the Grease Compositions

[0088] The grease compositions described herein are useful for lubricating, sealing and protecting mechanical components such as gears, axles, bearings, shafts, hinges and the like. Such mechanical components are found in automobiles, trucks, bicycles, steel mills, mining equipment, railway equipment including rolling stock, aircraft, boats, construction equipment and numerous other types of industrial and consumer machinery. The grease compositions described herein may be used in various applications, including, but not limited to, lubricating surface mining machinery (pins and bushings, open gears in large electric shovels), constant velocity joints (CV joints), ball bearings, journal bearings, high speed low load machinery lubrication, low speed-high load machinery lubrication, conveyor belt bearings lubrication, gears lubrication, open gears lubrication, curve and
flange rail lubrication, traction motor gear lubrication, high temperature highly corrosive media lubrication, wheel bearing lubrication of motor vehicles and trucks, journal bearing lubrication of freight and high speed trains, paper machinery lubrication, lawn and garden machinery lubrication, pipe dope anti seize lubrication, automotive tie rod ends, roof, seating and steering mechanism lubrication, jacks and landing gear equipment lubrication, continuous caster and hot mills bearing lubrication, lubrication of garage door mechanisms and oven chain lubrication.

Grease Preparation

Greases can be manufactured in several consistencies as defined by National Lubricating Grease Institute (N.L.G.I.) as described in ASTM Method D-217 for Cone Penetration of Lubricating Greases. Adjusting the lubricating base oil, thickener component, and additive content will permit the manufacture of various grades of greases.

As is well known in the art, greases are sold in various grades depending upon the softness of the grease. The softer the grease, the more fluid the grease. For example, very soft greases sold under the designation NLGI 0 have a cone penetration number from about 355 to 385, those having a cone penetration range of 310 to 340 are designated NLGI 1 and the most widely sold greases have a cone penetration range of 265 to 295 and are designated NLGI 2. Table 1 below shows the various NLGI grades for greases.

<table>
<thead>
<tr>
<th>NLGI Grade</th>
<th>Worked Cone Penetration (ASTM D 217) @ 77° F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>445-475</td>
</tr>
<tr>
<td>00</td>
<td>400-430</td>
</tr>
<tr>
<td>0</td>
<td>355-385</td>
</tr>
<tr>
<td>1</td>
<td>310-340</td>
</tr>
<tr>
<td>2</td>
<td>265-295</td>
</tr>
<tr>
<td>3</td>
<td>220-250</td>
</tr>
<tr>
<td>4</td>
<td>175-205</td>
</tr>
<tr>
<td>5</td>
<td>130-160</td>
</tr>
<tr>
<td>6</td>
<td>85-115</td>
</tr>
</tbody>
</table>

Since there are a variety of different greases with varying formulations and properties and since such properties can be altered, sometimes significantly, by changes in process conditions and apparatus, a great deal of flexibility is needed in the process equipment for manufacturing greases. Because of the desired flexibility and because many greases are specialty type greases made in small amounts, most grease manufacturing has been of the batch type.

Batch processing generally comprises the use of one or more large kettles that may be equipped with, for example, paddle agitation, stirring, heating, external recirculation systems capable of pumping the contents from the bottom of the kettle to the top, and combinations thereof. The kettles that may be utilized herein may be of a size generally in a range of from 500 liters to 20,000 liters, preferably in a range of from 2,000 liters to 15,000 liters, and more preferably in a range of from 3,000 liters to 10,000 liters. Examples of suitable kettles include open kettles and pressurized kettles. An example grease kettle is equipped with stirring, heating, and an external recirculation system, capable of pumping the contents from the bottom of the kettle to the top. The kettles may have heating means, cooling means, paddle type stirrers, gear-type circulation pumps, circulation line, back pressure shear valve in said circulation line, colloid mill, product filter, and other associated piping, valves, instrumentation, etc. required for the commercial manufacture of grease. The grease may also be passed through a grease mill again to obtain a further improvement in yield and appearance, where such mills may include a Morehouse mill, a Charlotte mill, and a Guiolin homogenizer.

Another type of batch processor sometimes used is a Strato® mixer which has a different internal mixing configuration. In this equipment, the material is circulated by an impeller located at the bottom of the vessel, where it is possible to obtain rapid circulation and thorough mixing.

To prepare the simple greases described herein, the various thickener components (one or more of: carboxylic acids, hydrogenated natural oil, and/or hydrogenated methylenized natural oil derivative) are added to a lubricating base oil, and this mixture is charged to a kettle, mixer, or equivalent vessel. Preferably, these thickener components are naphthenic acid, 12-hydroxy stearic acid, hydrogenated castor oil, and hydrogenated methylenized soybean oil (S60), and the lubricating base oil is a naphthenic pale oil. These materials are then stirred and heated to a temperature between about 140° F. to 200° F. for approximately 30-60 minutes, in order to dissolve one or more of the acids into the lubricating base oil. The metal base, usually a metal hydroxide such as lithium hydroxide is then charged to the vessel, usually in an amount slightly in excess of the stoichiometric amount required to neutralize the acid. The temperature at this stage is usually between about 190° F. to about 270° F., preferably between about 240° F. to about 260° F., for a period of time (approximately 30-90 minutes) sufficient to complete the neutralization and to effect a substantial dehydration of the mixture, i.e., the removal of 70 to 100% of the water, by venting. After venting the water vapor, heating of the mixture is resumed and increased to about 350° to about 430° F., preferably between about 390° F. to about 410° F., and maintained at that level for about 15 minutes to about 1 hour to ensure optimum soap crystallization, dispersing the acid into the mixture, and improved yields. This increase in temperature (or “cookout”) is effected as rapidly as possible to save time and to minimize oxidation.

Thereafter, the mixture is then transferred to a finishing kettle or equivalent vessel for cooling. This cooling is assisted by incorporating additional lubricating base oil into the mixture. Mixing can be continued until the grease reaches ambient temperatures. After about 90 minutes into this cooling phase, the heat is removed, and at about 1 hour thereafter, optional grease additives may be added to the finishing kettle.

In some embodiments, the grease compositions described herein may also encompass complex greases. Complex greases are formed by reaction of a metal-containing reagent with two or more acids. One of the acids is (i) a hydroxy carboxylic acid or reactive derivative thereof, such as a C9-C24 hydroxy stearic acid, preferably 9-hydroxy, 10-hydroxy, or 12-hydroxy stearic acid, or the mono- or diesters or poly-ester thereof, and (ii) a dicarboxylic acid, such as one or more straight or branched chain C2-C12 dicarboxylic acids, examples of which may include oxalic, malonic, succinic, glutaric, adipic, suberic, pimelic, azeladic, dodecanedioic and sebacic acids, preferably azelaic acid, or the mono- or di-esters or poly-esters thereof. Optionally, an additional hydroxy carboxylic acid may be utilized, where such acid has from 3 to 14 carbon atoms and can be either an
aliphatic acid such as lactic acid, 6-hydroxy decanoic acid, 3-hydroxybutanoic acid, 4-hydroxybutanoic acid, etc. or an aromatic acid such as parahydroxybenzoic acid, salicylic acid, 2-hydroxy-4-hexylbenzoic acid, meta hydroxybenzoic acid, 2,5-dihydroxybenzoic acid; 2,6-dihydroxybenzoic acid; 4-hydroxy-3-methoxybenzoic acid, etc. or a hydroxyaromatic aliphatic acid such as orthohydroxyphenyl, metahydroxyphenyl, or parahydroxyphenyl acetic acid. A cycloaliphatic hydroxy acid such as hydroxy cyclopentyl carboxylic acid or hydroxynaphthenic acid could also be used. There is no absolute industry standard defining the dropping point of a complex grease. However, it is often accepted that minimum dropping points of about 260° C. are displayed by complex greases. Generally, a complex grease is one which displays a dropping point significantly higher, typically at least about 20° C. higher, than the corresponding simple metal soap grease.

To prepare the complex greases described herein, the various thickener components (one or more of: carboxylic acids, hydrogenated natural oil, and/or hydrogenated natural oil derivative) are added to a lubricating base oil, and this mixture is charged to a kettle, mixer, or equivalent vessel. Preferably, these thickener components are naphthenic acid, 12-hydroxystearic acid, azelaic acid, and hydrogenated metathesized soybean oil (S60), and the lubricating base oil is a naphthenic pale oil. These materials are then stirred and heated to a temperature between about 140° F. to 200° F. for approximately 30-60 minutes, in order to dissolve one or more of the acids into the lubricating base oil. The metal base, usually a metal hydroxide such as lithium hydroxide is then charged to the vessel, is then added to convert the azelaic acid to its diol metal soap (dilithium azelate) usually in an amount slightly in excess of the stoichiometric amount required to neutralize both acid groups of the azelaic acid. The temperature at this stage is usually between about 190° F. to about 270° F., preferably between about 240° F. to about 260° F., for a period of time (approximately 30-90 minutes) sufficient to complete the neutralization and to effect a substantial dehydration of the mixture, i.e., the removal of 70 to 100% of the water, by venting. After venting the water vapor, heating of the mixture is resumed and increased to about 350° F. to about 430° F., preferably between about 390° F. to about 410° F., and maintained at that level for about 15 minutes to about 1 hour to ensure optimum soap crystallization, dispersing of the acid into the mixture, and improved yields. This increase in temperature (or “cookout”) is effects as rapidly as possible to save time and to minimize oxidation.

Thereafter, the mixture is then transferred to a finishing kettle or equivalent vessel for cooling. This cooling is assisted by incorporating additional lubricating base oil into the mixture. Mixing can be continued until the grease reaches ambient temperatures. After about 90 minutes into this cooling phase, the heat is removed, and at about 1 hour thereafter, optional grease additives may be added to the finishing kettle.

In some embodiments, the S60 component of the thickener serves to liberate long chain (i.e. C18 and higher) dicarboxylate salts, carboxylate salts, and glycerol upon exposure to metal hydroxides during grease processing, thus serving as a latent grease complexing agent. Also, since the S60 component will often react in a similar manner to hydrogenated castor oil, simple greases may achieve some complex character under standard processing conditions (3 hours). The inclusion of S60 into simple grease compositions would allow for lower processing temperatures and increased production capacity without compensating simple grease performance.

To illustrate the chemistry involved in this application, a representative reaction between S60 and lithium hydroxide is shown below:
cessing temperatures lower than the melt point of 12-hydroxystearic acid (~400°F.) used to thicken simple lithium grease. Reduced thickener kettle reaction temperatures may reduce processing time and increase grease throughput depending on the manufacturing protocol.

[0102] While the invention as described may have modifications and alternative forms, various embodiments thereof have been described in detail. It should be understood, however, that the description herein of these various embodiments is not intended to limit the invention, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the claims. Further, while the invention will also be described with reference to the following non-limiting examples, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art, particularly in light of the foregoing teachings.

EXEMPLARY EXAMPLES

Example 1

[0103] In a 100 gallon Stratco® mixer vessel, various thickener components were added. In this step, naphthenic acid (0.2% by weight), 12-hydroxystearic acid (4.9% by weight), hydrogenated castor oil (1.9% by weight), and S60 (1% by weight), were added to Pale Oil 750 (lubricating base oil), and melted into the lubricating base oil at 170°F. and mixed. After 50 minutes, aqueous lithium hydroxide was charged to the vessel, and the mixture heated to about 250°F. to a nearly fluid consistency, to saponify and neutralize this mixture. Thereafter, water vapor was vented upon reaction completion, and heating was increased to about 380°F. to completely disperse the lithium 12-HSA into the mixture. This mixture was then transferred to a finishing kettle, at a period between 60 and 90 minutes from the start of the experiment, an additional amount of lubricating base oil was added dropwise for dilution. At about 90 minutes, the heat was removed, and at about 1 hour thereafter, optional additives were charged to the finishing kettle, and cooling resumed until the end of the experiment at 4 hours.

[0104] It was determined that the inclusion of S60 in the thickener matrix at 1% by weight yielded a complex grease (NLGI grade 2-60 stroke unworked/worked cone penetration—267, 262; 10,000 stroke—270 dmm, 100,000 stroke—293 dmm; Timken 50 lb pass; drop point 514°F.).

Example 2

[0105] In a 100 gallon Stratco® mixer vessel, various thickener components were added. In this step, naphthenic acid (0.34% by weight), 12-hydroxystearic acid (7.32% by weight), azelaic acid (2.4% by weight), and S60 (1.5% by weight), were added to Pale Oil 750 (lubricating base oil), and melted into the lubricating base oil at 170°F. and mixed. After 50 minutes, aqueous lithium hydroxide was charged to the vessel, and the mixture heated to about 250°F. to a nearly fluid consistency, to saponify and neutralize this mixture. Thereafter, water vapor was vented upon reaction completion, and heating was increased to about 350°F. to completely disperse the lithium 12-HSA and azelaic acid into the mixture. This mixture was then transferred to a finishing kettle, at a period between 60 and 90 minutes from the start of the experiment, an additional amount of lubricating base oil was added dropwise for dilution. At about 90 minutes, the heat was removed, and at about 1 hour thereafter, optional additives were charged to the finishing kettle, and cooling resumed until the end of the experiment at 4 hours.

[0106] It was determined that the inclusion of S60 in the thickener matrix at 1.5% by weight yielded a complex grease (NLGI grade 2-60 stroke unworked/worked cone penetration—267, 262; 10,000 stroke—270 dmm, 100,000 stroke—293 dmm; Timken 50 lb pass; drop point 514°F.).

Example 3

[0107] In an open kettle, various thickener components were added. In this step, one or more components, such as naphthenic acid, 12-hydroxystearic acid, hydrogenated castor oil, and S60, in the percentages by weight shown in Table 2 below, were added to Pale Oil 750 (lubricating base oil), and melted into the lubricating base oil at 170°F. and mixed. After 50 minutes, aqueous lithium hydroxide was charged to the vessel, and the mixture heated to about 250°F. to a nearly fluid consistency, to saponify and neutralize this mixture. Thereafter, water vapor was vented upon reaction completion, and heating was increased to about 380°F. to completely disperse the lithium 12-HSA into the mixture. This mixture was then transferred to a finishing kettle, at a period between 60 and 90 minutes from the start of the experiment, an additional amount of lubricating base oil was added dropwise for dilution. At about 90 minutes, the heat was removed, and at about 1 hour thereafter, optional additives were charged to the finishing kettle, and cooling resumed until the end of the experiment at 4 hours.

[0108] The quantities of the lubricating base oil, thickener components, reaction conditions, and material properties of the finished simple greases and complex grease products are shown in Table 2.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Formulation</th>
<th>12-HSA (A) (% w/w)</th>
<th>H. Castor (G) (% w/w)</th>
<th>Naphthenic Acid (% w/w)</th>
<th>Azelaic Acid (% w/w)</th>
<th>Total Thickener (% w/w)</th>
<th>S60 (% w/w)</th>
<th>Final Reaction Temp (°F)</th>
<th>Drop Point (°F)</th>
<th>Cone Penetr. (dmm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>1.95</td>
<td>1.92</td>
<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>0</td>
<td>400</td>
<td>386</td>
<td>279</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>1.95</td>
<td>1.92</td>
<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>1</td>
<td>400</td>
<td>406</td>
<td>390</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>1.95</td>
<td>1.92</td>
<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>0</td>
<td>350</td>
<td>369</td>
<td>324</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>1.95</td>
<td>1.92</td>
<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>1.5</td>
<td>350</td>
<td>367</td>
<td>311</td>
</tr>
<tr>
<td>5</td>
<td>A</td>
<td>1.95</td>
<td>1.92</td>
<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>2</td>
<td>350</td>
<td>371</td>
<td>470</td>
</tr>
</tbody>
</table>
### TABLE 2-continued

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Formulation</th>
<th>12-HSA (A) (w/w)</th>
<th>H. Castor (G) (w/w)</th>
<th>Napthenic Acid (w/w)</th>
<th>Azelaic Acid (w/w)</th>
<th>Total Thicker (w/w)</th>
<th>S60 (w/w)</th>
<th>Final Reaction Temp (°F)</th>
<th>Drop Point (°F)</th>
<th>Cone Penet (dmm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>A</td>
<td>6.18</td>
<td>2.32</td>
<td>0.16</td>
<td>0.00</td>
<td>8.66</td>
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<td>341</td>
<td>450</td>
</tr>
<tr>
<td>8</td>
<td>A</td>
<td>7.50</td>
<td>2.70</td>
<td>0.16</td>
<td>0.00</td>
<td>10.16</td>
<td>0.00</td>
<td>350</td>
<td>379</td>
<td>243</td>
</tr>
<tr>
<td>9</td>
<td>B</td>
<td>6.83</td>
<td>0.00</td>
<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>1.5</td>
<td>350</td>
<td>392</td>
<td>322</td>
</tr>
<tr>
<td>10</td>
<td>B</td>
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<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>0.00</td>
<td>350</td>
<td>π</td>
<td>na</td>
</tr>
<tr>
<td>11</td>
<td>B</td>
<td>6.83</td>
<td>0.00</td>
<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>1.5</td>
<td>350</td>
<td>π</td>
<td>na</td>
</tr>
<tr>
<td>12</td>
<td>B</td>
<td>6.83</td>
<td>0.00</td>
<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>1.5</td>
<td>350</td>
<td>π</td>
<td>na</td>
</tr>
<tr>
<td>13</td>
<td>B</td>
<td>6.83</td>
<td>0.00</td>
<td>0.16</td>
<td>0.00</td>
<td>6.99</td>
<td>2.00</td>
<td>350</td>
<td>366</td>
<td>464</td>
</tr>
<tr>
<td>14</td>
<td>C</td>
<td>7.32</td>
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<td>2.4</td>
<td>10.06</td>
<td>1.5</td>
<td>350</td>
<td>351</td>
<td>267</td>
<td></td>
</tr>
</tbody>
</table>

Compared to control experiment 3, inclusion of S60 at 1% (experiment 4) and 1.5% (experiment 5) enabled grease formation at near NLGI Grade 2 specification at 350°F. At 2% S60 (experiment 6), the grease was extremely soft, suggesting a threshold level had been exceeded. Control (experiment 7) showed that the increased relative amount of 12-hydroxystearic acid and hydrogenated castor oil in the thickener (about 8% by weight) did not allow processing at 350°F. Control (experiment 8) showed that the increased relative amount of 12-hydroxystearic acid and hydrogenated castor oil in the thickener (about 10% by weight) produced a harder grease at NLGI Grade 3 specification. A pilot scale run at 350°F for experiment 5 yielded at NLGI specification grease (drop point of 378°F, unworked/worked cone penetration of 326/324 dmm). A pilot scale run at 350°F for experiment 14 successfully yielded a complex grease at 350°F. Experiment 9 also showed that a simple grease may be made without the inclusion of hydrogenated castor oil, which produced a grease at NLGI Grade 1 specifications.

**What is claimed is:**

1. A grease composition comprising:
   
   (a) from 50 to 99 weight percent of a lubricating base oil, and
   
   (b) from 1 to 30 weight percent of a thickener component comprising one or more of (i) one or more natural oil derivatives, (ii) one or more hydrogenated metathesized natural oils and/or natural oil derivatives, (iii) one or more amidated metathesized natural oils and/or natural oil derivatives, (iv) one or more carboxylic acids and/or derivatives thereof; and (v) one or more of a metal base compound; and
   
   (c) from 1 to 15 weight percent of one or more optional additives.

2. The grease composition of claim 1, wherein the lubricating base oil comprises a mineral oil, a synthetic oil, a natural oil, or a natural oil derivative, individually or in combinations thereof.

3. The grease composition of claim 1, wherein the natural oil derivative is a hydrogenated natural oil selected from the group consisting of hydrogenated canola oil, hydrogenated rapeseed oil, hydrogenated coconut oil, hydrogenated corn oil, hydrogenated cottonseed oil, hydrogenated olive oil, hydrogenated palm oil, hydrogenated peanut oil, hydrogenated safflower oil, hydrogenated sesame oil, hydrogenated soybean oil, hydrogenated sunflower oil, hydrogenated linseed oil, hydrogenated palm kernel oil, hydrogenated tung oil, hydrogenated jatropha oil, hydrogenated mustard oil, hydrogenated canola oil, hydrogenated pennycress oil, hydrogenated castor oil, hydrogenated animal fat, individually or in combinations thereof.

4. The grease composition of claim 3, wherein the hydrogenated natural oil is hydrogenated castor oil.

5. The grease composition of claim 1, wherein the one or more hydrogenated metathesized natural oils and/or natural oil derivatives comprises a hydrogenated metathesized natural oil selected from the group consisting of hydrogenated metathesized canola oil, hydrogenated metathesized rapeseed oil, hydrogenated metathesized coconut oil, hydrogenated metathesized corn oil, hydrogenated metathesized cottonseed oil, hydrogenated metathesized olive oil, hydrogenated metathesized palm oil, hydrogenated metathesized peanut oil, hydrogenated metathesized safflower oil, hydrogenated metathesized sesame oil, hydrogenated metathesized soybean oil, hydrogenated metathesized sunflower oil, hydrogenated metathesized linseed oil, hydrogenated metathesized palm kernel oil, hydrogenated metathesized tung oil, hydrogenated metathesized jatropha oil, hydrogenated metathesized mustard oil, hydrogenated metathesized camellia oil, hydrogenated metathesized pennycress oil, hydrogenated metathesized castor oil, hydrogenated metathesized animal fat, individually or in combinations thereof.

6. The grease composition of claim 1, wherein the one or more hydrogenated metathesized natural oils and/or natural oil derivatives comprises an amidated hydrogenated metathesized soybean oil based wax.

7. The grease composition of claim 1, wherein the one or more amidated metathesized natural oils and/or natural oil derivatives comprises an amidated hydrogenated metathesized soybean oil based wax.

8. The grease composition of claim 1, wherein the one or more carboxylic acids and/or derivatives thereof comprises a C2-C36 mono-, di-, tri-, and/or poly-carboxylic acid and/or derivative thereof.

9. The grease composition of claim 8, wherein the C2-C36 mono-, di-, tri-, and/or poly-carboxylic acid and/or derivative thereof comprises a hydroxy-substituted, aliphatic, cyclic, alicyclic, aromatic, branched, saturated, unsaturated, or heteroatom substituted, carboxylic acid or ester derivative thereof.

10. The grease composition of claim 8, wherein the C2-C36 mono-, di-, tri-, and/or poly-carboxylic acid and/or derivative thereof comprises a C12-C24 hydroxy carboxylic acid or C12-C24 hydroxy ester derivative of such acids.

11. The grease composition of claim 10, wherein the C12-C24 hydroxy carboxylic acid or ester derivative of such acids is 12-hydroxystearic acid and ester derivatives.
12. The grease composition of claim 10, wherein the C_{12}-C_{24} hydroxy carboxylic acid ester derivative is 12-hydroxy-stearate.

13. The grease composition of claim 8, wherein the C_{2}-C_{36} mono-, di-, tri-, and/or poly-carboxylic acid comprises a C_{2} to C_{12} aliphatic dicarboxylic acid.

14. The grease composition of claim 13, wherein the C_{2} to C_{12} aliphatic dicarboxylic acid comprises azelaic acid.

15. The grease composition of claim 1, wherein said metal base compound is a metal hydroxide selected from the group consisting of calcium hydroxide, strontium hydroxide, lithium hydroxide, sodium hydroxide, potassium hydroxide, and magnesium hydroxide.

16. The grease composition of claim 1, wherein said optional additives are selected from the group consisting of: metal deactivators, antioxidants, antiwear agents, rust inhibitors, viscosity modifiers, extreme pressure agents, and corrosion inhibitors.

17. A process for preparing a simple grease composition comprising the steps of:

(a) adding from 1 to 30 weight percent of a thickener component comprising one or more of (i) one or more natural oil derivatives, (ii) one or more hydrogenated metathesized natural oils and/or natural oil derivatives, (iii) one or more amidated metathesized natural oils and/or natural oil derivatives, (iv) one or more carboxylic acids and/or derivatives thereof, to from 50 to 99 weight percent of a lubricating base oil, and charging this mixture to a kettle, mixer or equivalent vessel;

(b) heating the mixture from step (a) to a temperature between about 140°F to 200°F for approximately 30-60 minutes, in order to dissolve the one or more carboxylic acids and/or derivatives thereof into the lubricating base oil;

(c) charging one or more of a metal base compound to the kettle, mixer or equivalent vessel, in an amount slightly in excess of the stoichiometric amount required to neutralize the two or more carboxylic acids and/or derivatives thereof;

(d) maintaining the conditions of step (c) at a temperature between about 190°F to about 270°F for approximately 30-90 minutes to complete the neutralization and to effect a substantial dehydration of the mixture of step (c);

(e) heating the mixture from step (d) to about 350°F to about 430°F for up to approximately 60 minutes;

(f) cooling the mixture from step (e) with the assistance of incorporating an additional amount of the lubricating base oil and the removal of heat, to yield the grease composition; and

(g) adding from 1 to 15 weight percent of one or more optional additives to the grease composition.

18. A process for preparing a complex grease composition comprising the steps of:

(a) adding from 1 to 30 weight percent of a thickener component comprising one or more of (i) one or more natural oil derivatives, (ii) one or more hydrogenated metathesized natural oils and/or natural oil derivatives, (iii) one or more amidated metathesized natural oils and/or natural oil derivatives, (iv) two or more carboxylic acids and/or derivatives thereof, to from 50 to 99 weight percent of a lubricating base oil, and charging this mixture to a kettle, mixer or equivalent vessel;

(b) heating the mixture from step (a) to a temperature between about 140°F to 200°F for approximately 30-60 minutes, in order to dissolve the two or more carboxylic acids and/or derivatives thereof into the lubricating base oil;

(c) charging one or more of a metal base compound to the kettle, mixer or equivalent vessel, in an amount slightly in excess of the stoichiometric amount required to neutralize the two or more carboxylic acids and/or derivatives thereof;

(d) maintaining the conditions of step (c) at a temperature between about 190°F to about 270°F for approximately 30-90 minutes to complete the neutralization and to effect a substantial dehydration of the mixture of step (c);

(e) heating the mixture from step (d) to about 350°F to about 430°F for up to approximately 60 minutes;

(f) cooling the mixture from step (e) with the assistance of incorporating an additional amount of the lubricating base oil and the removal of heat, to yield the grease composition; and

(g) adding from 1 to 15 weight percent of one or more optional additives to the grease composition.

19. A grease composition comprising:

(d) from 89 to 93 weight percent of a lubricating base oil,

(e) from 6 to 11 weight percent of a thickener component comprising one or more of (i) one or more natural oil derivatives, (ii) one or more hydrogenated metathesized natural oils and/or natural oil derivatives, (iii) one or more amidated metathesized natural oils and/or natural oil derivatives, (iv) one or more carboxylic acids and/or derivatives thereof, (v) one or more of a metal base compound; and

(f) from 1 to 15 weight percent of one or more optional additives selected from the group consisting of: metal deactivators, antioxidants, antiwear agents, rust inhibitors, viscosity modifiers, extreme pressure agents, and corrosion inhibitors.