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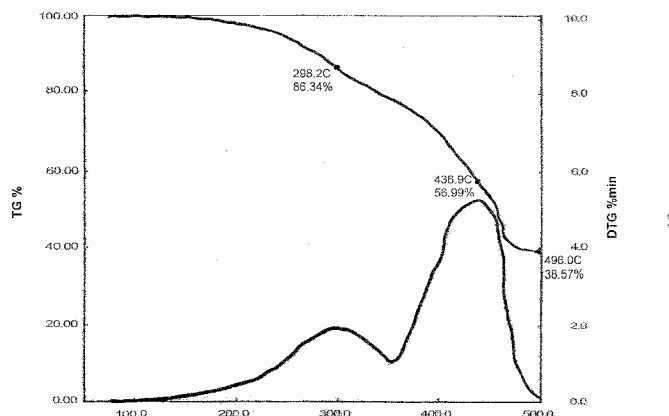


Fig. 1

(57) Abstract: Shelf stable, flowable liquids of overbased alkaline earth metal salts are prepared by reacting an alkaline earth metal base and a carboxylic acid in the presence of a hydrocarbon liquid, a polyol and an alcohol. The resulting overbased alkaline earth metal salts have an alkaline earth metal content of at least about 14.5% and a non-volatile matter content of at least about 95%.

OVERBASED METAL CARBOXYLATE PRECURSOR AND PROCESS FOR MAKING

[0001] This international patent application claims priority to U.S. Patent Application Serial No. 12/106,358, filed April 21, 2008.

[0002] The invention relates to a shelf stable, flowable liquid of an alkaline earth metal salt of a fatty acid and a process for preparing the liquid. More particularly, the invention relates to a shelf stable, flowable precursor of an overbased alkaline earth metal carboxylate and a process for preparing the precursor. Even more particularly, the invention relates to a shelf stable, flowable precursor of an overbased calcium carboxylate and a process for preparing the precursor.

BACKGROUND OF THE INVENTION

[0003] The preparation of overbased calcium or barium salts of carboxylic acids, alkyl phenols, and sulfonic acids are disclosed in the following U.S. Pat. Nos. 2,616,904; 2,760,970; 2,767,164; 2,798,852; 2,802,816; 3,027,325; 3,031,284; 3,342,733; 3,533,975; 3,773,664; and 3,779,922. The use of these overbased metal salts in the halogen-containing organic polymer is described in the following U.S. Pat. Nos. 4,159,973; 4,252,698; and 3,194,823. The use of overbased barium salt in stabilizer formulations has increased during recent years. This is due, in the main, to the fact that overbased barium salts possess performance advantages over the neutral barium salts. The performance advantages associated with overbased barium salts are low plate-out, excellent color hold, good long-term heat stability performance, good compatibility with the stabilizer components, etc. Unfortunately, most of the overbased barium salts are dark in color and, while these dark colored overbased barium salts are effective stabilizers for halogen-containing organic polymer, their dark color results in the discoloration of the end product. This feature essentially prohibits the use of dark colored overbased barium salts in applications where a light colored polymer product is desired.

[0004] According to the teachings of U.S. Pat. No. 4,665,117, light colored alkali or alkaline earth metal salts are prepared where alkyl phenol is used as a promoter. However, alkyl phenol is also a major cause for the development of color in the final product. This problem is

overcome by the use of propylene oxide which displaces the hydrogen of the phenolic hydroxyl group and thereby restricts the formation of colored species. However, there are disadvantages associated with this approach, principally due to the toxic nature of propylene oxide. Propylene oxide is classified as a possible carcinogen and laboratory animal inhalation studies have shown evidence of a link to cancer. Propylene oxide is also listed as a severe eye irritant, and prolonged exposure to propylene oxide vapors may result in permanent damage to the eye. Furthermore, propylene oxide is extremely flammable and explosive in nature under certain conditions. Propylene oxide boils at 94 °F and flashes at -20 °F. As a result, extreme precautions are required to handle propylene oxide at the plant site. Special storage equipment is required for propylene oxide and other safety features are necessary. U.S. Pat. No. 4,665,117 describes the use of propylene oxide at 150 °C. At this temperature, propylene oxide will be in the gaseous phase. Under these operating conditions, more than stoichiometric amounts of propylene oxide are required to carry the reaction to completion because propylene oxide will escape from the reaction mixture and this requires additional handling of the excess propylene oxide.

[0005] Liquids of overbased metal carboxylate salts are also used in the preparation of greases. In particular, grease manufacturing includes a multi-step process and numerous additives to provide property enhancements which present an increasing challenge to the specialty, food-grade and bio-based grease formulators. The resulting grease performance is also strongly dependent upon the processing conditions such as temperature, pressure, residence times and saponification stoichiometry.

[0006] Thixotropic greases or grease-like overbased metal carboxylate or other overbased metal-containing compositions having corrosion-inhibiting properties, and having utility for a variety of uses such as, for instance, in automobile and truck body undercoatings, and for various other purposes, are known to the art. Such greases or grease-like compositions have gone into quite widespread use either as such, or admixed with other ingredients to produce compositions for use in a variety of environments, and, generally speaking, they are characterized by reasonably good extreme pressure and antiwear properties, high dropping points, reasonably good resistance to mechanical breakdown, salt spray and water-corrosion resistance, thermal stability at high temperatures, and other desirable properties.

[0007] Whether the liquid of an overbased metal carboxylate salt is utilized in halogen-containing organic polymers or in the preparation of greases, volatile components, including

volatile organic compounds (VOCs), of the overbased metal carboxylate should be minimized for health, safety and environmental reasons.

[0008] Notwithstanding the state of the art as described herein, there is a need for further improvements in preparing overbased alkaline earth metal salts of fatty acids for use in halogen-containing organic polymers and in the preparation of greases, wherein the overbased alkaline earth metal salts have substantially reduced levels of volatile components within the final product.

SUMMARY OF THE INVENTION

[0009] In general, one aspect of the invention is to provide a shelf stable liquid of an overbased alkaline earth metal salt of a fatty acid, wherein the alkaline earth metal content is at least about 14.5% and the non-volatile matter content is at least about 95%.

[0010] In yet another aspect of the invention, a shelf stable, flowable liquid of an overbased alkaline earth metal salt of a fatty acid is provided. The liquid includes at least one hydrocarbon liquid, a polyol, an alcohol, wherein the alcohol has at least 8 carbon atoms, and an overbased alkaline earth metal salt of a fatty acid, wherein the alkaline earth metal salt has an alkaline earth metal content of at least about 14.5% and a non-volatile matter content of at least about 95%.

[0011] In another aspect of the invention, a method for preparing a shelf stable, flowable liquid of an overbased alkaline earth metal salt of a fatty acid is provided. the method includes the steps of:

(a) preparing a precursor mixture comprising a carboxylic acid, wherein the carboxylic acid is a fatty acid; at least one hydrocarbon liquid; a polyol; and an alcohol, wherein the alcohol has at least 8 carbon atoms;

(b) neutralizing the carboxylic acid with an initial amount of alkaline earth metal base to form an alkaline earth metal carboxylate precursor mixture;

(c) heating the alkaline earth metal carboxylate precursor mixture;

(d) adding an additional amount of an alkaline earth metal base to the alkaline earth metal carboxylate precursor mixture;

(e) carbonating the precursor mixture to neutrality;

(f) filtering the precursor mixture; and

(g) distilling the precursor mixture until an alkaline earth metal content of at least about 14.5% and a non-volatile matter content of at least about 95% is achieved.

[0012] These and other advantages and novel features of the present invention, as well as details of an illustrated embodiment thereof, will be more fully understood from the following description.

BRIEF DESCRIPTION OF THE DRAWING

[0013] FIG. 1 is a graph of a thermogravimetric analysis of a shelf stable, flowable liquid of an overbased alkaline earth metal salt of a fatty acid in one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0014] In one embodiment of invention, a shelf stable, flowable liquid of an overbased alkaline earth metal salt of a fatty acid prepared from a precursor includes an alkaline earth metal carbonate, an alkaline earth metal carboxylate of a fatty acid, a liquid hydrocarbon, and an alcohol having at least 8 carbon atoms, with the liquid having alkaline earth metal content is at least about 14.5% and the non-volatile matter content is at least about 95%.

[0015] The alkaline earth metal of the salt of the overbased alkaline earth metal salt of the fatty acid precursor may be selected from the group consisting of calcium, barium, magnesium and strontium. These metals may be derived from metal oxides and hydroxides, and in some instances, metal sulfides and hydrosulfides. For example, the alkaline earth metal salt may include a calcium carboxylate.

[0016] The carboxylic acid portion of the overbased alkaline earth metal salt precursor may include fatty acids, including C₈-C₃₀ saturated, unsaturated carboxylic acids of 8 to 30 carbon atoms, either alone or in combination with each other, or reactive equivalents of carboxylic acids. Examples of useful carboxylic acids and fatty acids include but are not limited to caprylic acid, capric acid, lauric acid, myristic acid, myristoleic acid, 2-ethylhexanoic acid, decanoic acid, dodecanoic acid, pentadecanoic acid, palmitic acid, palmitoleic acid, stearic acid, 12-hydroxystearic acid, oleic acid, ricinoleic acid, linoleic acid, linoleic acid, arachidic acid, gadoleic acid, behenic acid, erucic acid, and mixtures of any of these acids.

[0017] The shelf stable, flowable liquid of an overbased alkaline earth metal salt of the fatty acid precursor of the present invention may also include an alcohol that promotes the formation of the overbased alkaline earth metal carboxylate. The alcohol includes aliphatic

alcohols that contain at least 8 carbon atoms. In one example, an aliphatic alcohol having a range from about 8 to about 18 carbon atoms may be used. Examples of such aliphatic alcohols include isodecanol, dodecanol, octanol, tridecanol, tetradecanol or mixtures thereof. It has been found that when a higher aliphatic alcohol is employed in making the overbased product, phenol may be excluded from the reaction as a promoter.

[0018] The shelf stable liquid of an overbased alkaline earth metal salt of the fatty acid precursor of the present invention may also include a polyol. The polyol can be a glycol or glycol ether. The glycol or glycol ether may be selected from the group consisting of diethylene glycol monobutyl ether (butyl Carbitol®), triethylene glycol, hexylene glycol, propylene glycol, dipropylene glycol, diethylene glycol monomethyl ether, ethylene glycol monobutyl ether, and mixtures thereof.

[0019] In another embodiment of the present invention, a liquid base oil may also be employed for preparing the overbased precursor materials. The base oil can be a hydrocarbon liquid that generally includes any hydrocarbon diluent. Most generally, the liquid hydrocarbon is selected from the group of hydrocarbon oils, mineral spirits, non-aromatic hydrocarbons and polyalphaolefins (PAOs). In one embodiment of the invention, suitable hydrocarbon liquids include SHELLSOL™ D70 and D80 commercially available from Shell Chemical. In yet another embodiment, the PAOs are utilized, either alone or in combination with other liquid hydrocarbons, as suitable liquid hydrocarbons for preparing the overbased precursor material since they have flexible alkyl branching groups on every other carbon of their polymer backbone chain. These alkyl groups, which can shape themselves in numerous conformations, make it very difficult for the polymer molecules to line themselves up side-by-side in an orderly way. Furthermore, many PAOs are relatively stable at higher temperatures and typically have a tendency not to crystallize or solidify at lower temperatures since they are able to remain as oily, viscous liquids.

[0020] In yet another embodiment of the invention, the process for preparing a shelf stable liquid of an overbased alkaline earth metal salt of a fatty acid precursor includes reacting an alkaline earth metal base and a fatty acid with an equivalent ratio of metal base to the fatty acid being greater than 1:1 in the presence of at least one liquid hydrocarbon, an alcohol, and a glycol ether. The mixture may be acidified and carbonated to produce amorphous alkaline earth metal carbonate within the mixture. During carbonation, a dispersion may be added containing

alkaline earth metal base, liquid hydrocarbon and an alcohol having at least 8 carbon atoms in relative amounts at a controlled rate of base addition to produce a stable haze free liquid reaction product. During the reaction, water is removed from the reaction product to produce a shelf stable, flowable liquid overbased alkaline earth metal salt. Generally, the entire process may be conducted in the absence of free oxygen and, for this purpose, an atmosphere of nitrogen may be used.

[0021] Throughout this specification and claims, the term "basic" or "overbased" as applied to the alkaline earth metal salts is used to refer to metal compositions wherein the ratio of total metal contained therein to the fatty acid moieties is greater than the stoichiometric ratio of the neutral metal salt. That is, the number of metal equivalents is greater than the number of equivalents of the fatty acid. In some instances, the degree to which excess metal is found in the basic metal salt is described in terms of a "metal ratio". Metal ratio as used herein indicates the ratio of total alkaline earth metal in the oil-soluble composition to the number of equivalents of the fatty acid or organic moiety. The basic metal salts often have been referred to in the art as "overbased" or "superbased" to indicate the presence of an excess of the basic component.

[0022] It has been found important during carbonation to add the dispersion of metal base, liquid hydrocarbon and aliphatic alcohol in relative amounts at a controlled rate to produce the stable reaction product. There are a number of reasons which are believed to contribute to the formation of a stable liquid which is then filterable to remove impurities and byproducts of the reaction. It has been determined that by the continuous addition of the dispersion or slurry of base during carbonation, such results are achievable. It is believed that the metal base slurry prevents the formation of undesirable calcium carbonate crystals or byproducts in the desired overbased metal salt. These undesirable moieties prevent the formation of stable products which are filterable. Thus, the metal base slurry is added at a controlled rate which does not exceed the rate of the desired product-forming reaction. The reaction is controlled by continuous or incremental addition of the metal base to make the calcium ions immediately available for the desired reaction as opposed to allowing the metal base, for example lime, to react and form a byproduct. Excessive byproduct or lime coated with calcium carbonate is believed to render the liquid product unfilterable. Using this procedure, the pH is controlled during the reaction so that the fatty acid is neutralized and the pH rises to about 7-10 with the continued addition of base to produce dissolved metal ion which reacts with CO₂ during carbonation to produce the desired

product. It is believed if the reaction rate is not controlled, and the base is not dissolved, then solid base reacts or is coated with calcium carbonate to form undesirable byproducts. The formation of undesirable byproducts of the reaction renders the final product unstable and unfilterable.

[0023] As developed above, one of the features of the method is the step of adding during carbonation a dispersion of an alkaline earth metal base, polyol, liquid hydrocarbon and an alcohol having at least 8 carbon atoms at a controlled rate of base addition to produce the stable, flowable liquid. It has been determined that the addition of a dispersion of the base in the liquid hydrocarbon and aliphatic alcohol protects or passivates the base, thereby enabling the formation of a stable, flowable liquid reaction product. By protecting or passivating the base, carbonation proceeds to produce amorphous alkaline earth metal carbonate. Unexpectedly, the reaction proceeds without the need to remove water during the reaction and results in a shelf stable liquid reaction product.

[0024] The amount of alkaline earth metal base utilized in the preparation of basic salts is an amount which is more than one equivalent of the base per equivalent of fatty acid or organic moiety, and more generally, will be an amount sufficient to provide at least three equivalents of the metal base per equivalent of the acid. Larger amounts can be utilized to form more basic compounds, and the amount of metal base included may be any amount up to that amount which is no longer effective to increase the proportion of metal in the product. When preparing the mixture, the amount of fatty acid and the alcohol included in the mixture should be greater than 1:1 in order to provide a basic product. More generally, the ratio of equivalents will be at least 3:1.

[0025] The ratios of hydrocarbon oil to alcohol (dodecanol) are about 2:1 to about 4:1 in one embodiment of the invention. The glycol ether may be used at about 1-15% of the final product.

[0026] The lime slurry which is added to the oleic acid in the reaction is formulated to be a pumpable mixture with the general composition of about 40-50% lime, about 25-40% hydrocarbon oil, about 10-25% dodecanol, and about 0-10% propylene glycol. The propylene glycol amount that is needed to make a pumpable slurry increases as the percentage of lime in the slurry increases.

[0027] The process for preparing the shelf stable, flowable overbased calcium carboxylate precursor includes the reaction of an alkaline earth metal base and a carboxylic acid to form an alkaline earth metal carboxylate mixture, with an equivalent ratio of metal base to the carboxylic acid greater than 1:1 in the presence of a liquid hydrocarbon, an aliphatic alcohol, and a glycol ether. In one embodiment, the carboxylic acid is a fatty acid, the fatty acid being oleic acid, the liquid hydrocarbon is SHELLSOL™ D80, the alcohol is dodecanol, and the glycol ether is propylene glycol. The mixture is acidified, through a process of carbonation, to produce amorphous alkaline earth metal carbonate, for example calcium carbonate. The step of carbonation involves treating the mixtures described above with an acidic gas in the absence of free oxygen until the titratable basicity is determined using phenolphthalein. Generally, the titratable basicity is reduced to a base number below about 10. The mixing and carbonation steps require no unusual operating conditions other than the exclusion of free oxygen.

[0028] By the term "acidic gas" as used in this specification and in the claims is meant a gas which upon reaction with water will produce an acid. Thus, such gases as sulfur dioxide, sulfur trioxide, carbon dioxide, carbon disulfide, hydrogen sulfide, etc., are exemplary of the acidic gases which are useful in the preparation of the overbased metal carboxylates disclosed. When carbon dioxide is used the alkaline earth carbonate is formed. When the sulfur gases are used, the sulfate, sulfide and sulfite salts are formed.

[0029] During carbonation, the alkaline earth metal base, polyol, liquid hydrocarbon and alcohol may be added in relative amounts at a controlled rate of base addition. In one embodiment of the invention, the dry alkaline earth metal base, polyol, liquid hydrocarbon and alcohol may be slurried to facilitate mixing during the carbonation process. Water is removed from the reaction product to produce a shelf stable, flowable liquid of an alkaline earth metal salt of a fatty acid. Generally, the process be conducted in the absence of free oxygen and, for this purpose, an atmosphere of nitrogen is used.

[0030] During carbonation the mixture may be heated to a temperature which is sufficient to drive off some of the water contained in the mixture or the water generated during the reaction of the base and the carboxylic acid can be retained during the overbasing reactions. The treatment of the mixture with the carbon dioxide preferably is conducted at elevated temperatures, and the range of temperatures used for this step may be any temperature above ambient temperature in the range from about 75 °C (about 165 °F) to about 200 °C (about 390

°F). Higher temperatures may be used such as 250 °C (about 480 °F), but there is no apparent advantage in the use of such higher temperatures. Ordinarily, a temperature of about 80 °C (about 175 °F) to 150 °C (about 300 °F) is satisfactory.

[0031] Other features of the method include filtering the product of the reaction to produce a shelf stable liquid precursor at a product filtration rate of at least about 300 ml per 10 minutes. In one embodiment of the invention, the product which is produced is filterable to remove unwanted byproducts and enhance the shelf stability of the overbased liquid. For example, with a Buchner funnel under vacuum of about 25-30 inches Hg with a Whatman No. 1 filter and a diatomaceous earth filtering aid, the product is filterable at satisfactory rates. Thus, filtration removes undesirable impurities including silica, iron oxide and other metal species, unreacted calcium hydroxide, calcium carbonate, and other oxides which may contribute to lack of stability.

[0032] In another aspect of the invention, the liquid overbased alkaline earth salt of the fatty acid precursor is believed to be a thermodynamically stable microemulsion. The microemulsion has micelles and a continuous phase. The micelles consist of an alkaline earth metal carbonate and an alkaline earth metal carboxylate of the fatty acid. The continuous phase of the microemulsion consists of the liquid hydrocarbon and the alcohol.

[0033] In yet another embodiment of the invention, after the removal of water from the precursor of the alkaline earth metal base, fatty acid, polyol, liquid hydrocarbon and alcohol, the precursor is distilled or vacuum stripped at a temperature up to about 165 °C (about 330 °F) to remove the volatile components of the reaction product. In distillation terminology, "stripping" refers to the removal of a volatile component from a less volatile substance. The vacuum stripping proceeds until the final product has a measured alkaline earth metal content of at least about 14.5% and a non-volatile matter content of at least about 95%.

[0034] In still yet another embodiment of the invention, the vacuum stripping of the precursor yielded an unexpected result. In particular, it was previously believed that in order to maintain a stable microemulsion of the liquid overbased alkaline earth salt of the fatty acid, the liquid hydrocarbon and alcohol components of the continuous phase were both necessary in the final reaction product. However, it was unexpectedly observed that upon subjecting the precursor to vacuum stripping, not only did the final product maintain its shelf stable and

flowable liquid properties, but it was determined that the final product had a final non-volatile matter content of at least 95% and a flash point of greater than 93 °C (about 200 °F).

[0035] The reaction mixture for an overbased calcium oleate, after addition of the slurry and carbonation with carbon dioxide and after vacuum stripping, has the following composition ranges:

Calcium oleate about 15-40% by weight

Calcium carbonate about 9-35% by weight

Hydrocarbon oil about 25-35% by weight

Dodecanol (co-surfactant) less than about 5% by weight

Propylene glycol less than about 1% by weight

[0036] Substitution of magnesium, strontium, or barium for calcium in the overbased salt is done on an equivalent basis of the metal hydroxide. On the basis of the final reaction mixture prior to vacuum stripping, the following amounts may be used:

Ca(OH)_2 (lime) about 15-35% by weight

Mg(OH)_2 about 12-24% by weight

Sr(OH)_2 about 25-50% by weight

Ba(OH)_2 about 35-50% by weight

[0037] The following Examples illustrate the preparation of the shelf stable haze free liquids of the overbased salts in accordance with the method of the present invention, but these examples are not considered to be limiting the scope of this invention. Unless otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, and all temperatures are in degrees Fahrenheit.

EXAMPLES

Formation of Overbased Calcium Oleate Precursor I

Example 1

[0038] A 15% overbased calcium oleate/carbonate was prepared according to this Example. A mixture of about 274.3 g of oleic acid, about 270.0 g of D-80, about 140.3 g of

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dodecanol, about 50.0 g of propylene glycol and about 25.0 g of water was heated to about 88 °C (about 190 °F), with stirring, under a nitrogen atmosphere. To the stirred mixture there was continuously added a dispersion comprised of about 140.4 g of D-80, about 85.0 g of dodecanol, about 25.0 g of propylene glycol and about 276.7 g of lime for about 50 minutes to produce a solution of calcium oleate in the mixture. At this point in the reaction, the mixture tested basic with phenolphthalein (about 10-12 pH). Then, to the stirred mixture there was continuously added, over a period of about 3 hours, the mixture was treated with carbon dioxide at 1.5 SCFH at about 93 °C (about 200 °F). The basicity of the reaction was checked to maintain the basicity during the reaction. When the reaction mixture tested nearly neutral to phenolphthalein, the carbon dioxide addition was discontinued. The reaction mixture was then heated to about 149 °C (about 300 °F). and a total of 85.2 g of water was removed via a Dean-Stark trap. The resulting product mixture was stirred and 24.00 g of filter aid (diatomaceous earth) was added. The product mixture was filtered with suction, as stated above in the description, at over 500 ml per 10 minutes, yielding a shelf stable, flowable liquid filtrate of overbased calcium oleate/carbonate which remained shelf stable upon cooling to room temperature.

Vacuum Stripping of Overbased Calcium Oleate Precursor I

Example 2

[0039] A 250 ml three neck round bottom flask was charged with the precursor obtained in Example 1. The three neck round bottom flask was then fitted with a nitrogen inlet to sparge the mixture in one neck of the flask, a temperature probe in another neck of the flask and a vacuum line in the other neck of the flask. The vacuum filtration was conducted at a temperature between about 149 °C (about 300 °F) and about 163 °C (about 325 °F) with the nitrogen gas supplied at a rate of 6 cubic feet per hour (SCFH). A total distillate of about 678.6 g was collected yielding a non-volatile matter content of about 84.2% and the filtrate was analyzed to contain about 14.8% calcium by weight. After the addition of about 50.0 g 6.0 cSt PAO to the mixture, further vacuum filtration was conducted as described above. After an additional three hours of filtration, it was determined that the mixture had a non-volatile matter content of about 99.4% and the filtrate was analyzed to contain about 15.7% calcium by weight. The final product had the following physical properties:

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Flash point - > 200 °C (about 392 °F)

Specific gravity – about 1.162

Weight per gallon – 9.68

% Volatile by volume - < 1

% Volatile by weight - < 1

As seen in FIG. 1, a graph of a thermogravimetric analysis (TGA) of the vacuum-stripped final product is provided. The analysis was conducted using a Seiko 5200 TG/DTA. The sample was evaluated from about 30 °C (about 86 °F) to about 550 °C (about 1022 °F) at a rate of 10 °C/min. The thermogram (TG%) of the final product shows the decomposition of the final product as a function of temperature. The weight loss profiles, as designated by inflection points on the TG% curve of the final product, were determined to be 86.3% at 298.2 °C (about 568 °F), 56.99% at 436.9 °C (about 819 °F) and 38.6% at 496.0 °C (about 925 °F). The inflection points represent a point or temperature on a curve at which the curvature of the plot changes sign during the decomposition of the various components of the final product, including various forms of calcium carbonate including calcite, vaterite and/or aragonite if present. The inflection points are represented by the first derivative curve (DTG %/min). These results suggest that the vacuum-stripped final product of the shelf stable, flowable overbased alkaline earth salt of the fatty acid has a non-volatile matter content greater than 95% when measured at 200 °C (about 392 °F).

Formation of Overbased Calcium Oleate Precursor II

Example 3

[0040] A 15% overbased calcium oleate/carbonate was prepared according to this Example. A mixture of about 274.3 g of oleic acid, about 270.0 g of D-80, about 140.3 g of dodecanol, about 50.0 g of propylene glycol, about 100.0 g of 6.0 cSt PAO and about 25.0 g of water was heated to about 88 °C (about 190 °F), with stirring, under a nitrogen atmosphere. To the stirred mixture there was continuously added a dispersion comprised of about 140.4 g of D-80, about 85.0 g of dodecanol, about 25.0 g of propylene glycol, about 50.0 g of 6.0 cSt PAO and about 277.0 g of lime for about 50 minutes to produce a solution of calcium oleate in the mixture. At this point in the reaction, the mixture tested basic with phenolphthalein (about 10-12 pH). Then, to the stirred mixture there was continuously added, over a period of about 3 hours,

the mixture was treated with carbon dioxide at 1.5 SCFH at about 93 °C (about 200 °F). The basicity of the reaction was checked to maintain the basicity during the reaction. When the reaction mixture tested nearly neutral to phenolphthalein, the carbon dioxide addition was discontinued. The reaction mixture was then heated to about 149 °C (about 300 °F), and a total of about 110.0 g of water was removed via a Dean-Stark trap. The resulting product mixture was stirred and 26.00 g of filter aid (diatomaceous earth) was added. The product mixture was filtered with suction, as stated above in the description, at about 1000 ml in about 5.5 minutes and about 1225 ml in about 7 minutes, yielding a shelf stable, flowable liquid filtrate of overbased calcium oleate/carbonate which remained shelf stable upon cooling to room temperature.

Vacuum Stripping of Overbased Calcium Oleate Precursor II

Example 4

[0041] The procedure according to Example 3 was repeated and the filtrate from both procedures, which resulted in a total of about 2,032 g of product, was combined and prepared for vacuum stripping. A three neck round bottom flask was charged with the precursor material obtained in the two preparations according to Example 3. The three neck round bottom flask was then fitted with a nitrogen inlet to sparge the mixture in one neck of the flask, a temperature probe in another neck of the flask and a vacuum line in the other neck of the flask. The vacuum filtration was conducted at a temperature between about 149 °C (about 300 °F) and about 163 °C (about 325 °F) with the nitrogen gas supplied at a rate of 6 cubic feet per hour (SCFH). About 7.5 hours into the vacuum stripping of the sample, the non-volatile matter content was determined to be about 95.3% and the filtrate was analyzed to contain about 15.7% calcium by weight. After the addition of about 25.0 g of 6.0 cSt polyalphaolefin (PAO) to the mixture, further vacuum filtration was conducted as described above. After an additional four hours of filtration, it was determined that the mixture had a non-volatile matter content of about 98.2% and the filtrate was analyzed to contain about 15.7% calcium by weight. An additional amount of about 45.0 g of 6.0 cSt PAO was added to the mixture in order to adjust the final calcium content measured to be about 15.3% calcium by weight. The final product had the following physical properties:

Flash point - > 200 °C (about 392 °F)

Specific gravity – about 1.144

Weight per gallon – 9.53

% Volatile by volume - < 1

% Volatile by weight - < 1

[0042] Based upon the foregoing disclosure, it should now be apparent that the overbased, shelf stable, flowable liquid of an alkaline earth metal salt of a fatty acid and a process for preparing the liquid as described herein will carry out the objects set forth hereinabove. It is, therefore, to be understood that any variations evident fall within the scope of the claimed invention and thus, the selection of specific component elements can be determined without departing from the spirit of the invention herein disclosed and described.

CLAIMS

What is claimed is:

1. A shelf stable, flowable liquid of an overbased alkaline earth metal salt of a fatty acid, the liquid comprising:
 - at least one hydrocarbon liquid;
 - a polyol;
 - an alcohol, wherein the alcohol has at least 8 carbon atoms; and
 - an overbased alkaline earth metal salt of a fatty acid, wherein the alkaline earth metal salt has an alkaline earth metal content of at least about 14.5% and a non-volatile matter content of at least about 95%.
2. The liquid of claim 1, wherein the fatty acid is a C₁₂-C₂₂ fatty acid.
3. The liquid of claim 2, wherein the fatty acid is oleic acid.
4. The liquid of claim 1, wherein an alkaline earth metal of the overbased alkaline earth metal salt is selected from the group consisting of calcium, barium, magnesium and strontium.
5. The liquid of claim 1, wherein the overbased alkaline earth metal salt is calcium oleate.
6. The liquid of claim 1, wherein the alcohol is an aliphatic alcohol of at least 14 carbon atoms.
7. The liquid of claim 1, wherein the polyol is a glycol or a glycol ether selected from the group consisting of diethylene glycol monobutyl ether, propylene glycol, hexylene glycol, triethylene glycol, dipropylene glycol, diethylene glycol monomethyl ether, ethylene glycol monobutyl ether, and mixtures thereof.
8. A method for preparing a shelf stable, flowable liquid of an overbased alkaline earth metal salt of a fatty acid, the method comprising the steps of:

(a) preparing a precursor mixture comprising a carboxylic acid, wherein the carboxylic acid is a fatty acid; at least one hydrocarbon liquid; a polyol; and an alcohol, wherein the alcohol has at least 8 carbon atoms;

(b) neutralizing the carboxylic acid with an initial amount of alkaline earth metal base to form an alkaline earth metal carboxylate precursor mixture;

(c) heating the alkaline earth metal carboxylate precursor mixture;

(d) adding an additional amount of an alkaline earth metal base to the alkaline earth metal carboxylate precursor mixture;

(e) carbonating the precursor mixture to neutrality;

(f) filtering the precursor mixture; and

(g) distilling the precursor mixture until an alkaline earth metal content of at least about 14.5% and a non-volatile matter content of at least about 95% is achieved.

9. The method of claim 8, wherein the fatty acid is a C₁₂-C₂₂ fatty acid.

10. The method of claim 9, wherein the fatty acid is oleic acid.

11. The method of claim 8, wherein the alkaline earth metal is selected from the group consisting of calcium, barium, magnesium and strontium.

12. The method of claim 8, wherein the alkaline earth metal carboxylate precursor mixture includes calcium oleate and calcium carbonate.

13. The method of claim 8, wherein the alcohol is an aliphatic alcohol of at least 12 carbon atoms.

14. The method of claim 8, wherein the polyol is a glycol or a glycol ether selected from the group consisting of diethylene glycol monobutyl ether, propylene glycol, hexylene glycol, triethylene glycol, dipropylene glycol, diethylene glycol monomethyl ether, ethylene glycol monobutyl ether, and mixtures thereof.

15. The method of claim 8, wherein the precursor mixture is distilled with vacuum stripping.
16. A shelf stable, flowable liquid of an overbased alkaline earth metal salt of a fatty acid, the liquid comprising:
 - at least one hydrocarbon liquid;
 - propylene glycol;
 - dodecanol; and
 - overbased calcium oleate, wherein the overbased calcium oleate has an alkaline earth metal content of at least about 14.5% and a non-volatile matter content of at least about 95%.
17. The liquid of claim 16, wherein the at least one liquid hydrocarbon liquid is selected from the group consisting of hydrocarbon oils, mineral spirits, non-aromatic hydrocarbons and polyalphaolefins (PAOs).
18. The liquid of claim 16, wherein the overbased calcium oleate has an alkaline earth metal content of at least about 15.0% calcium by weight.
19. The liquid of claim 16, wherein the liquid has a non-volatile matter content of at least about 97%.
20. The liquid of claim 16, wherein the liquid includes forms of calcium carbonate selected from the group consisting of calcite, vaterite and aragonite.

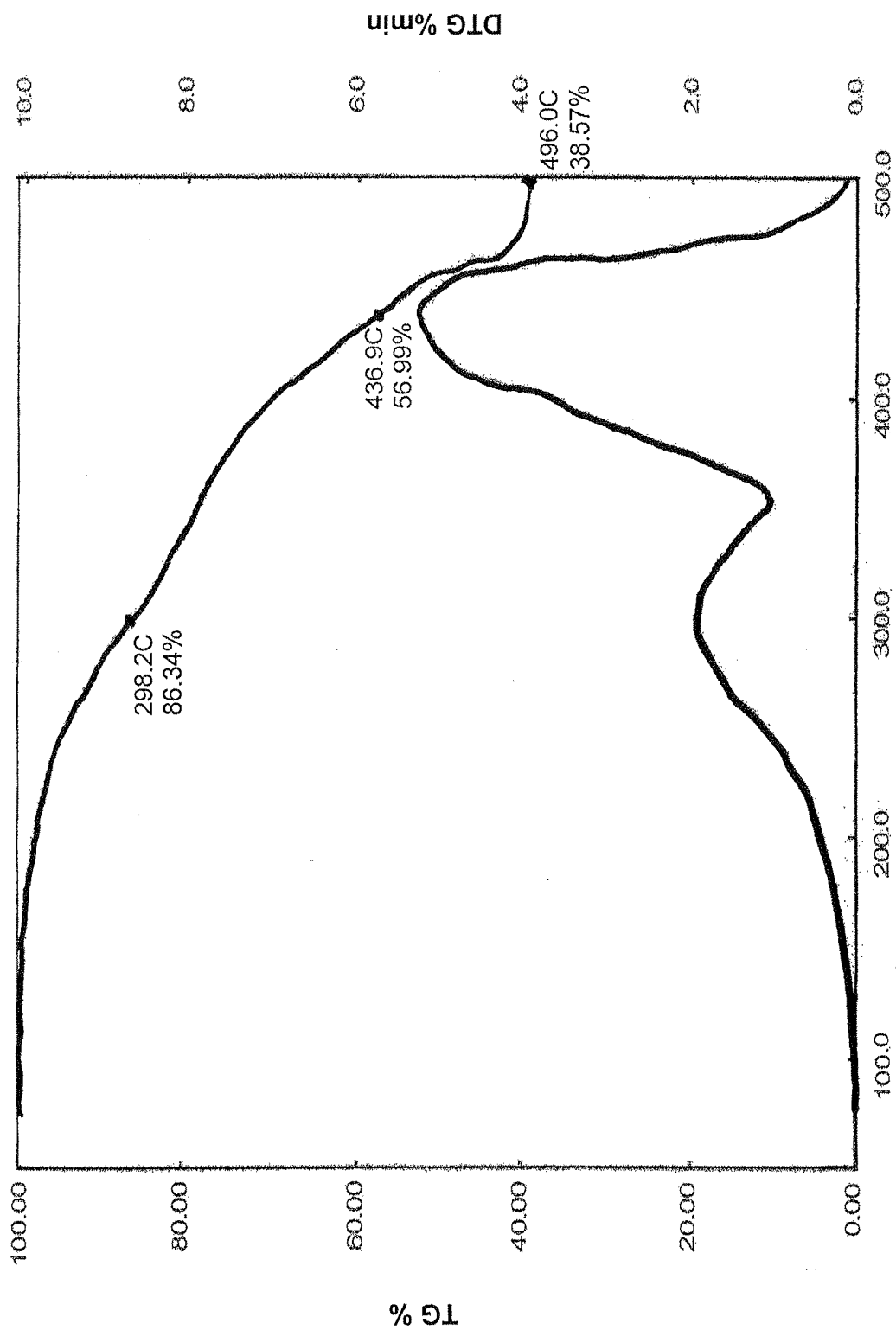


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/082724**A. CLASSIFICATION OF SUBJECT MATTER***C07F 3/04(2006.01)i, C07F 3/02(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC C07F, C08K, C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility models and applications for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS(KIPO internal), Google scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2004/0053795 A1 (James E. Reddy et al.) 18 March 2004 See [0013]-[0017], [0019]-[0021], [0023], [0036]], [0038], claims 1, 14, 26, 27, 41 and 42.	1-20
Y	US 2003/0104954 A1 (James E. Reddy et al.) 05 June 2003 See [0014], [0020]-[0023], [0025], [0036] and example 2.	1-20
Y	US 5,523,005 A (Stephen A. Di Biase et al.) 04 June 1996 See examples B-10 and B-18.	1-20
Y	US H1536 (Jack L. Karn et al.) 04 June 1996 See column 7 and example 1.	1-20
A	Umesh N.Choori et al., Removal of VolatileOrganic Compounds from Surfactant Solutions by Flash Vacuum Stripping in a Packed Column, Fall 1998 GWMR, Pages 157-165.	15

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 JUNE 2009 (26.06.2009)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2008/082724

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