Petroleum or hydrocarbon wax oxidate composition.

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Description

Field of the invention

This invention relates to a petrolatum or hydrocarbon wax oxidate composition and to a method for producing the same. More specifically, this invention relates to a petrolatum or hydrocarbon wax oxidate composition which comprises the reaction product of (a) a petrolatum or hydrocarbon wax oxidate, as described herein, or the metal salt thereof, with (b) a polyamine, as described herein, wherein the petrolatum or hydrocarbon wax oxidate composition has a very high viscosity, increased molecular weight and sinewy characteristics.

Background of the invention

Oxidized petroleum fractions, which fractions include waxes and petrolatums, are known as a source of saponifiable material useful in the production of lubricating greases and in the formulation of protective coatings.

Highly oxidized petroleum fractions and processes for their production are described in U.S. Patents 4,186,077 and 4,198,285 of the inventor herein. Oxidation of petroleum fractions, e.g., petrolatums, utilizing the processing conditions described in these two U.S. patents provides oxidates having high viscosity, molecular weight and sinewy characteristics which have advantageous properties over oxidates produced in accordance with previous oxidation techniques.

US—A—3 038 815 discloses preparing amidation products of paraffin oxidates by the reaction of the oxidates with polyamines. The polyamines are used in amounts of from 7 to 22% by weight of the oxidate and the resulting products are actual amides. While oxidates produced conventionally and in accordance with the processes disclosed in the above described U.S. patents have advantageous properties, the viscosity, molecular weight and integrity of these oxidate products and the sinewy properties of said amidation products are not completely sufficient for all applications and improvements in these and other characteristics of oxidate products are desired.

Summary of the invention

Accordingly, an object of this invention is to provide a petrolatum or hydrocarbon wax oxidate composition having high viscosity.

Another object of this invention is to provide a petrolatum or hydrocarbon wax oxidate composition having an increased molecular weight.

A further object of this invention is to provide a process for producing the high-viscosity petrolatum or hydrocarbon wax oxidate composition.

An even further object of this invention is to provide a process for increasing the molecular weight and viscosity of a petrolatum or hydrocarbon wax oxidate.

Also, an object of this invention is to provide compositions containing the high-viscosity petrolatum or hydrocarbon wax oxidate composition where the compositions are useful as lubricants, greases, corrosion inhibitor compositions, protective coating compositions and the like.

These and other objects are achieved by the invention described herein.

In one embodiment of this invention, this invention provides a method of producing a petrolatum or hydrocarbon wax oxidate composition which method comprises reacting simultaneously or in any order: (a) a hydrocarbon wax oxidate, a petrolatum oxidate or a mixture of said hydrocarbon wax oxidate and said petrolatum oxidate, and (b) a polyamine having at least 2 amino groups, each group having at least 1 active hydrogen, characterized in that an amount from 0.04 to 7% by weight of the polyamine based on the weight of said oxidate is used whereby a sinewy or film-forming reaction product is obtained.

In a further embodiment of this invention, this invention provides a method for altering the characteristics of petrolatum or hydrocarbon wax oxidates or the metal salts thereof comprising forming the reaction product of; (a) a hydrocarbon wax oxidate, a petrolatum oxidate, or a mixture of said hydrocarbon wax oxidate and said petrolatum oxidate, with (b) a polyamine having at least 2 amino groups, each group having at least 1 active hydrogen atom; or a metal salt of said reaction product, by reacting, in any order, said oxidate (a) and said polyamine (b) and, if necessary, forming said metal salt prior to or subsequent to said reacting of said oxidate (a) and said polyamine (b), characterized in that the polyamine is used in an amount from 0.04 to 7% by weight of the weight of said oxidate, whereby a sinewy or film-forming reaction product is obtained.

An even further embodiment of this invention provides a method for altering the characteristics of petrolatum or hydrocarbon wax oxidates or the metal salts thereof comprising reacting the petrolatum and/or hydrocarbon wax oxidate or metal salt thereof with a polyamine having at least two amino groups, in which each amino group has at least one active hydrogen atom.

Detailed description of the invention

In this invention, the starting material used is a hydrocarbon wax oxidate and/or a petrolatum oxidate or a metal salt thereof. Such a hydrocarbon wax oxidate basically comprises the oxidation product having a
high acid number obtained on oxidizing a petrolatum, a hydrocarbon wax or a mixture of a petrolatum and a hydrocarbon wax.

Exemplary petrolatum and hydrocarbon wax starting materials and techniques for producing by oxidation the petrolatum or hydrocarbon wax oxide used in this invention are described in U.S. Patent 4,186,077 and U.S. Patent 4,198,286, issued to the inventor.

Particularly, suitable hydrocarbon feed stocks which can be used and oxidized to obtain the petrolatum or hydrocarbon wax oxide suitable for use in this invention are hydrocarbons comprising a mixture of straight and branched chain saturated hydrocarbons having on the average 20 to 100 carbon atoms per molecule. In particular, preferred petrolatums and hydrocarbon waxes which can be oxidized to produce a particularly useful starting material in this invention are petrolatums containing about 40 to about 100 carbon atoms and hydrocarbon waxes containing about 20 to about 44 carbon atoms.

Suitable petrolatums and/or hydrocarbon wax oxides which can be used in this invention can be appropriately prepared by oxidizing these hydrocarbon feed stocks as described above using processes known in the art. Such a petrolatum or hydrocarbon wax oxide has been oxidized to a sufficient extent to be suitable for use herein if the oxide has an acid number of about 20 to about 150, preferably about 40 to about 50 for a petrolatum oxide and about 80 to about 100 for a hydrocarbon wax oxide. For mixtures of hydrocarbon waxes and petrolatum oxides, a suitable acid number will be generally proportional to the proportion of the hydrocarbon wax oxide and the petrolatum oxide present. As used herein, the term “acid number” is defined to mean the number of milligrams of potassium hydroxide required to neutralize 1 gram of sample.

As described above, the hydrocarbon wax or petrolatum starting material is simply oxidized using conventional known techniques, for example, using conventional redox catalysts such as manganese salts. Further, the technique disclosed in U.S. Patent 4,186,077, in which an oxide is obtained by blowing an oxidizing gas through a liquid mass of the hydrocarbon in the presence of an amine oxide under the conditions as described therein, can be used. Alternatively, an oxide appropriate for use in this invention can be obtained by oxidizing a hydrocarbon in accordance with the procedure described in U.S. Patent 4,198,286 by blowing an oxidizing gas through a liquid mass of the hydrocarbon in the presence of a sulfobetaine.

To produce the high viscosity oxidation composition of this invention, it is only necessary to react the oxidate with a polyamine having at least two amino groups in which each of the groups has at least one active hydrogen atom.

Suitable polyamines which can be employed include diamines, triamines, tetramines, pentamines and higher polyamines. For simplicity in the disclosure hereinafter, the term “polyamine” will be employed to describe suitable amines which can be employed having at least two amino functional groups, each group of which has at least one active hydrogen atom. Specific examples of appropriate polyamines which can be employed include aliphatic and alicyclic polyamines such as monoethylamine (MEDA), diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), sym-dimethylethylene diamine, hexamethylenediamine (HMDA), N,N-dimethylhexamethylene diamine, 1,3-(or 1,2-)diaminopropane, 1,4-diaminobutane, 1,2-diaminocyclohexane, 1,10-dianodesapane, 1,12-dianodesanodecane, 1,7-diepine, 1,3-diamino - N - (5 - hydroxyethyl) - propane, 1,3-diamino - 2 - hydroxypropene, 1,5-diaminopentane, 1,8-diaminooctane, 1,2 - diamino - 2 - methylpropane, 1,8 - diamino - p - menthan, diaminoalcohol, N-methylethylene diamine, N,N-ethylethylene diamine, N,N,N,N-diethyl - 2 - butene, 1,4 - diamine, m-xylene diamine, 1,6-hexane diamine, N,N,N,N-dimethyl - 1,6 - hexane diamine, 2,5 - dimethyl - 2,5 - hexane diamine, and the like, aromatic polyamines such as o- (or m- or p-)phenylene diamine, 4,5 - dimethyl - o - phenylene diamine, 2,4- (or 2,6- or 3,4-)diaminotoluene, 4 - chloro - m - phenylene diamine, 3,4- (or 3,5-)diaminobenzic acid, 4,4-diaminodiphenyl amine, 3,4-diaminobenzophenone, 4,4’-diaminostilbene, 3,3’-diaminobenzidine, 2,5-diaminobenzensulfonic acid, 4,4’- methylenedianiline, 1,2- (or 1,4-; 1,5- or 2,6-)diaminoanthraquinone, 3,6-diaminocaridine, 4,5-diaminoacene, 2,3- (or 2,7-)diaminofluorene, 1,2- (or 1,5-; 1,8- or 2,3-)diaminophthalene, 9,10-diaminophanthenan, 1,8 - diamino - 4,5 - dihydroxyxanthraquinone, 4 - methoxy - o - phenylene diamine, 4,4’-diaminodiphenyl ether and the like, and heterocyclic polyamines such as 2,3- (or 2,6- or 3,4-)diaminopyridine, 3,5 - diamino - 2,6 - dimethoxyryridine, N - (2 - aminothyl) - piperidina, 4 - (aminomethyl) - piperidina, 4 - amino - 2,2,6,6 - tetramethylpiperidina, 5-aminoindole, 6-aminoindoline, 4 - amino - 5 - aminomethyl - 2 - methylpyrimidina, 4,5 - diamino - 6 - hydroxyururymidina, 4,6 - diamino - 5 - nitropyrimidina, 4,5- (or 4,6-)diaminopyrymidina, 2,4,5,6-tetraaminopyrimidina, 2-aminozimimidazole, 3,4 - diamino - 5 - hydroxyazepino, 3,5 - diamino - 1,2,4 - triazina, piparazine, and the like. Triethylen tetramine (TETA), diethylen triamine (DETA), tetraethylene pentamine (TEPA), piperazine, hexamethylenediamine (HMDA), monoethylenediamine (MEDA) are preferred with tetraethylene pentamine being particularly preferred. Polyfunctional amino
group containing nitrogen compounds from hydrogenated coal or shale oil can also be used as the polyamine.

From the above, it can be basically said that any polyamine having at least two amino groups in which each amino group contains at least one active hydrogen atom can be used as the polyamine in this invention. Other amino groups can be present as long as the polyamine has at least two amino groups as described above.

The reaction of the oxide with the polyamine can be conducted at a temperature of room temperature (e.g., 20 to 30°C) to a temperature just below the point at which the reactants would be thermally degraded, generally 21°C (70°F) to 177°C (350°F), more generally 93 to 121°C (200 to 250°F) under atmospheric pressure. Subatmospheric pressure or superatmospheric pressure can also be used, if desired.

The time of reaction for the polyamine with the oxide is not critical and will vary depending on the reactants and the temperature employed. In general, an appropriate time of reaction can be determined by basically measuring the viscosity characteristics of the high viscosity oxide composition of this invention produced. In general, high viscosity oxide compositions of this invention have a viscosity of 10 to 2500 g/cm · sec (poises) more preferably 25 to 350 g/cm · sec (poises).

The oxide composition of this invention is considered to have a high-viscosity, i.e., a viscosity of 10 to 2500 g/cm · sec (poises) at 25°C, which is markedly higher than the viscosity range generally encountered in prior art hydrocarbon wax or petrolatum oxides of 0.1 to 200 g/cm · sec (poises) at 25°C and for the calcium salts thereof of 2 to 80 g/cm · sec (poises) at 25°C. Further, the viscosity of the oxide composition of this invention can be adjusted by addition thereto of appropriate additives such as compatible solvents, if desired.

As indicated above, in one embodiment of this invention, by reacting the oxide with a polyamine, the characteristic that the oxidation process prior to reaction with the polyamine are altered. For example, the viscosity of the oxide used as a starting material is as indicated above and as can be seen from the viscosity range set forth above for the oxide reaction products, the viscosity of the composition is markedly increased. Further, the oxide reaction product has more sinewy characteristics than the oxide starting material. Increasing clarity and consistency are often obtained with the compositions of this invention. Where the composition of this invention is used as a protective coating or film, freedom from film graininess, improved film drying, improved film cohesiveness and improved corrosion and weather resistance are achieved.

In the reaction between the polyamine and the oxide, an appropriate ratio of the oxide to the polyamine is 0.01% by weight to 10% by weight, more preferably 0.05% by weight to 7% by weight, of the polyamine based on the weight of the oxide.

The reaction product of the oxide with the polyamine of this invention can be advantageously employed to produce greases, lubricants, corrosion inhibitor compositions, protective coatings, etc. Particularly, the oxide reaction product is capable of forming a film which is free of graininess, which is cohesive and which does not crack. Accordingly, use of such a grease or lubricant for machinery, automobiles, aircraft, marine craft, etc., as protective coatings for such or as a corrosion resistant composition to protect any type of metal surface from, e.g., oxidation, or other alteration, is particularly advantageous. The oxide composition of this invention is useful in protecting metal surfaces from the effects of salt spray, humidity, and like external conditions which without such protection deleterious effects on the metal surfaces arise.

As indicated above, the oxide of this invention can comprise the reaction product of a hydrocarbon wax oxide with a polyamine or the metal salt of the reaction product of the oxide and the polyamine. Where metal salts (sometimes designated a “soap”) are desired, any basic metal salt can be used. Suitable metal salts include those of lithium, sodium, potassium, magnesium, rubidium, strontium, cesium, barium, cadmium, aluminum, tin, bismuth, zinc and mixtures thereof. Preferred salts, particularly for protective coating film applications, are zinc and calcium salts and appropriate basic calcium and zinc salts such as calcium hydroxide, calcium oxide, zinc oxide and the like can be used. Calcium salts of the reaction product of this invention are particularly useful in preparing relatively firm, dry and non-tacky protective coating films and zinc salts of the reaction product of this invention are particularly useful in preparing softer protective coating films.

Where the metal salt oxide reaction product is desired, the oxide as a starting material can be reacted with the metal salt forming compound and then with the polyamine as described above or the reaction product of the oxide and the polyamine can be produced and then reacted with the basic salt described above in order to form the metal salt of the oxide composition. Appropriate reaction procedures for the formulation of the oxide reaction product in the metal salt form can be by simply mixing, in any order, the reactants, with stirring, the at room temperature to 204°C (400°F), more generally at 75°C (167°F) to 104°C (220°F).

A suitable amount of the compound for forming the salt to the oxide reaction product can range from 90% to 150% equivalence, preferably 100% to 125% equivalency, based on the acid number of the oxidation reaction product.

Alternatively, where the metal salt oxide reactant product is desired, the metal salt forming compound, the oxide starting material and the polyamine can all be combined and reacted
simultaneously to obtain the salt of the oxidate reaction product. Where a simultaneous reaction is accomplished, appropriate parameters can be selected from those given above.

Conventional additives such as petroleum sulfonates, thickeners, organic clays, pigments and the like for known purposes and in conventional amounts can also be added to the compositions of this invention to produce a broad range of different types of useful products.

The following examples are given to illustrate the present invention in greater detail. These examples are to be construed as merely exemplary and non-limiting. Unless otherwise indicated, all parts, percents, ratios, and the like are by weight.

### Example 1

A hydrocarbon wax oxidate with an acid number of 91.0, produced by conventionally oxidizing a hydrocarbon wax starting material was used. Light petroleum naphtha (226.0 grams) was placed in a 1 liter beaker and stirred. 14.1 (0.381 eq.) of lime, in a powder form, was drenched into the naphtha with continuous mixing to form a lime slurry. The lime slurry was heated to 65°C (150°F) and 235 grams (0.381 eq.) of the hydrocarbon wax oxidate described above was melted and slowly added thereto with stirring with the temperature being maintained at 104—110°C (220—230°F). The hydrocarbon wax containing slurry was kept at this temperature for one half hour with stirring and then allowing to cool to room temperature. A slight foaming was observed along with a slight thickening and darkening of the color of the composition. No deposition of lime was noted at the bottom of the beaker initially but over a period of time, settling of lime was observed. The mixture obtained was slightly grainy, cloudy and thinning with some lime fallout and possibly some sub-reaction product dropout.

#### Example 2

The same procedures as set forth in Comparative Example 1 were repeated except that 11.5 grams (0.381 eq.) of ethylene diamine was added to the mixture immediately after the hydrocarbon wax oxidate was added.

Some foaming was observed and the temperature increased rapidly to 82 to 102°C (180—216°F). After cooling, the mixture had a high viscosity and was very thick. The product was so thick that it was difficult to scrape off the stirrer and was found to be insoluble in toluene and water. No lime or soap fallout was observed.

#### Example 3

The same procedures as set forth in Comparative Example 1 were repeated except that 16.4 grams (0.381 eq.) of piperazine was added right after the hydrocarbon wax oxidate addition. A slight foaming was observed but no significant temperature increase was observed.

The mixture formed on cooling was very thick and had a high viscosity. No lime or soap fallout was observed.

#### Example 4

The procedures of Example 1 were repeated except that the lime addition was omitted. The temperature of the mixture immediately increased from 75 to 107°C (170 to 225°F) with a thickening of the viscosity. The mixture darkened and a slight foaming was observed. An extremely thick product was obtained.

#### Example 5

The procedures of Comparative Example 1 were repeated except that 14.4 grams (0.381 eq.) of tetraethylene pentamine was added just after the lime addition. A slight increase in temperature from 95 to 107°C (210 to 225°F) occurred.

A sudden thickening and viscosity increase were observed with some small amount of foam. No lime or soap fallout was observed.

The product obtained was extremely viscous to the extent that when 150 grams of the product obtained, which was non-flowable, was mixed with 130 grams of light petroleum naphtha, the product still was extremely viscous.

#### Example 6

The procedures of Example 4 were repeated except that no lime was employed. After adding the first few grams of the tetraethylene pentamine, a salt was formed but such disappeared after the addition of the remainder of the tetraethylene pentamine. The temperature increased to 115°C (240°F) and the mixture became thick with some foaming observed. A very high viscosity product was obtained.

#### Example 7

The procedures of Example 1 were used except that no lime was employed and instead of the hydrocarbon wax oxidate having an acid number of 91.0 and a saponification number of 200.4 was employed and mixed with 150 cc of mixed xylenes rather than the light petroleum naphtha. 9.2 grams
(0.243 eq. based on the five functional groups in the tetraethylene pentamine) of tetraethylene pentamine was employed and such was azeotropically distilled with the xylene to remove water. 5.5 cc of water in 6 hours was obtained and the water, when tested with litmus paper, was essentially neutral. The product obtained was a very nice gel.

Example 7
The same procedure as described in Example 1 above was repeated using 150 grams (0.243 eq.) of the same type of hydrocarbon wax oxidate as employed in Example 1 and 150 cc of mixed xylenes. To this, was added 0.5 grams (0.018 eq.) of tetraethylene pentamine and azeotropic distillation was conducted. 2.0 cc of water was obtained in the first three hours and 0.3 cc of water after 6 additional hours. The mixture was a gel-like solid at room temperature demonstrating the thickening effect of the amine.

Example 8
The same procedures of Example 7 were repeated except that an azeotropic distillation was conducted on the hydrocarbon wax oxidate/xylene mixture prior to addition of the amine with 1.8 cc of water being obtained in about an hour and 0.6 cc of water being obtained after 3 additional hours. Then, 0.067 grams (0.002 eq.) of tetraethylene pentamine were added and, on azeotropic distillation, less than 0.1 cc of water was obtained in 3.5 hours.

The mixture was a gel-like solid at room temperature demonstrating the thickening effect of the amine.

Examples 9—13
The same procedures were repeated as in Example 8 above, using various polyamines and in various amounts as set forth in the following table.

In each case, the reaction product obtained was gel-like at room temperature.

<table>
<thead>
<tr>
<th>Example</th>
<th>Polyamine</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Tetraethylene pentamine</td>
<td>6.6 g (0.243 eq.)</td>
</tr>
<tr>
<td>10</td>
<td>Triethylene tetramine</td>
<td>5.9 g (0.243 eq.)</td>
</tr>
<tr>
<td>11</td>
<td>Diethylene triamine</td>
<td>5.0 g (0.243 eq.)</td>
</tr>
<tr>
<td>12</td>
<td>Ethylene diamine</td>
<td>3.7 g (0.243 eq.)</td>
</tr>
<tr>
<td>13</td>
<td>Tetraethylene pentamine</td>
<td>3.3 g (0.122 eq.)</td>
</tr>
</tbody>
</table>

Example 14
150 g (0.243 eq.) of a hydrocarbon wax oxidate having an acid number of 91.0 and a saponification number of 196.4 was mixed with 150 cc of mixed xylenes. The mixture was brought to reflux to remove water present in the hydrocarbon wax oxidate using a Dean-Stark trap. 1.6 cc of water, acidic to litmus, was obtained in 2 hours. 9.0 g (0.243 eq.) lime was added thereto and refluxing continued to collect 41 cc of water from the amine, a condensation reaction being conducted in 3—4 hours. The product obtained was a gel at room temperature but when warmed up could be poured. No lime or soap fallout was observed.

Comparative Example 2
1000 grams of a light petroleum naphtha was placed in a 4 liter beaker and 65.6 g (1.61 eq.) of zinc oxide was added to the beaker with stirring. The zinc oxide slurry was then heated to 85°C (185°F). The, 1000 g (1.16 eq.) of a hydrocarbon wax oxidate having an acid number of 90.5 was melted and slowly added to the zinc oxide slurry and the mixture was heated to 93 to 104°C (200 to 220°F) for 1 hour with stirring. The source of heat was then removed and the mixture was allowed to cool, with stirring to 49°C (120°F). The slurry initially had a white colour and then became coffee cream colored and then dark and subsequently dark and clear.

Example 15
1000 grams of the zinc salt of the hydrocarbon wax oxidate produced in Comparative Example 2 above was heated to 93°C (200°F) to which was added 3 g (0.3%) tetraethylene pentatamine with stirring and the temperature held at 93 to 104°C (200 to 220°F) for ½ hour. The mixture was removed from the heat and, with stirring, allowed to cool to 49°C (120°F).

Comparative Example 3
The procedures of Comparative Example 2 were repeated but using 15.4 g (0.38 eq.) of zinc oxide.
Example 16
The procedures of Example 15 were repeated but using 1000 g of the zinc salt of the hydrocarbon wax oxide produced in Comparative Example 3 above.

Comparative Example 4
The procedures of Comparative Example 2 were repeated but using 1000 g (0.80 eq.) of a 90:10 by weight mixture of a hydrocarbon wax oxideate and a petrolatum oxideate, the mixture having an acid number of approximately 45 and further, 32.7 g (0.80 eq.) of zinc oxide was employed.

Example 17
The procedures of Example 15 were repeated except that 1000 g of the zinc salt of the hydrocarbon wax oxideate/petrolatum oxideate produced in Comparative Example 4 above was employed.

Comparative Example 5
To a 4 liter beaker containing 1000 g of light petroleum naphtha, 49.9 g (120% of stoichiometric) of lime was added and the slurry heated to 65°C (150°F). To this, 1000 g of a molten mixture of a hydrocarbon wax oxideate and a petrolatum oxideate, the mixture having an acid number of 63.1, was added, with stirring and the mixture was heated to 39 to 104°C (200 to 220°F) for 1 hour. The mixture was removed from the source of heat and stirred for 5 minutes and allowed to cool, with stirring, to 49°C (120°F).

Example 18
276.1 g of the calcium salt of the hydrocarbon wax oxideate/petrolatum oxideate mixture produced in Comparative Example 5 above was employed and to this 0.28 g (0.1%) of tetraethylene pentaamine was added thereto prior to removal from the source of heat.

Comparative Examples 6—8 and Examples 19—25
Procedures similar to those described above were employed to produce calcium salts of hydrocarbon wax oxideates and to produce compositions of this invention further containing a polyamine reacted with calcium salts of the hydrocarbon wax oxideates. The components employed, their characteristics and amounts, and other various characteristics of the products produced are shown in Table 2 below.
<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>A.N.</th>
<th>Amine</th>
<th>Hydrocarbon wax oxidate</th>
<th>Amine amount</th>
<th>Lime amount</th>
<th>Reaction product characteristics</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g</td>
<td>g</td>
<td>Lime dropout</td>
<td>Physical appearance</td>
</tr>
<tr>
<td>C. Ex. 6</td>
<td>91.0</td>
<td>None</td>
<td></td>
<td>0</td>
<td>14.1</td>
<td>slight</td>
<td>slightly grainy</td>
</tr>
<tr>
<td>Ex. 19</td>
<td>91.0</td>
<td>H₂NCH₂CH₂NH₂</td>
<td></td>
<td>11.5</td>
<td>14.1</td>
<td>none</td>
<td>homogen.</td>
</tr>
<tr>
<td>Ex. 20</td>
<td>91.0</td>
<td>Piperazine</td>
<td></td>
<td>16.4</td>
<td>14.1</td>
<td>none</td>
<td>homogen.</td>
</tr>
<tr>
<td>Ex. 21</td>
<td>91.0</td>
<td>H₂NCH₂CH₂NH₂</td>
<td></td>
<td>11.5</td>
<td>0</td>
<td>none</td>
<td>homogen.</td>
</tr>
<tr>
<td>Ex. 22</td>
<td>91.0</td>
<td>TEPA</td>
<td></td>
<td>14.4</td>
<td>14.1</td>
<td>none</td>
<td>homogen.</td>
</tr>
<tr>
<td>Ex. 23</td>
<td>91.0</td>
<td>TEPA</td>
<td></td>
<td>14.4</td>
<td>0</td>
<td>none</td>
<td>homogen.</td>
</tr>
<tr>
<td>Ex. 24</td>
<td>91.0</td>
<td>TEPA</td>
<td></td>
<td>0.8</td>
<td>14.1</td>
<td>none</td>
<td>homogen.</td>
</tr>
<tr>
<td>Ex. 25</td>
<td>91.0</td>
<td>TEPA</td>
<td></td>
<td>1.0</td>
<td>14.1</td>
<td>none</td>
<td>homogen.</td>
</tr>
<tr>
<td>C. Ex. 7</td>
<td>91.0</td>
<td>Adogen 170D</td>
<td></td>
<td>15.2</td>
<td>6.8</td>
<td>none</td>
<td>homogen.</td>
</tr>
<tr>
<td>C. Ex. 8</td>
<td>91.0</td>
<td>Adogen 170D</td>
<td></td>
<td>20.6</td>
<td>6.8</td>
<td>none</td>
<td>homogen.</td>
</tr>
</tbody>
</table>

Note:
A.N. = Acid number.
Adogen 170D = a commercially available long chain primary monoamine produced by Ashland Chemical Company.
Aged viscosity was determined after about 24 hours.
Comparative Examples 9 and 10 and Examples 26—29

Using procedures similar to those described above, calcium salts of hydrocarbon wax oxidates were produced and various polyamines as indicated in Table 3 below in the amounts indicated in Table 3 below were reacted therewith to produce reaction products of the polyamines indicated in Table 3 below. The viscosity of the resulting products were obtained and are also shown in Table 3 below. 2-Ethlyhexyl amine, as a primary monoamine, was employed for comparative purposes to demonstrate further the effects of the polyamine as opposed to a primary monoamine.

<table>
<thead>
<tr>
<th>Comp. Ex. or Ex. No.</th>
<th>Amine additive</th>
<th>Equivalents of additive</th>
<th>Reaction temp. used for reaction product</th>
<th>Brookfield viscosity (CPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 rpm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 C. Ex. 9</td>
<td>None</td>
<td>None</td>
<td>93—66°C</td>
<td>5,600 5,200</td>
</tr>
<tr>
<td>Ex. 26</td>
<td>Ethylenediamine</td>
<td>0.157</td>
<td>93—66°C</td>
<td>164,000 120,000</td>
</tr>
<tr>
<td>Ex. 27</td>
<td>Tetraethylenepentamine</td>
<td>0.157</td>
<td>93—66°C</td>
<td>38,000 36,000</td>
</tr>
<tr>
<td>Ex. 28</td>
<td>Piperazine</td>
<td>0.157</td>
<td>93—66°C</td>
<td>45,000 44,000</td>
</tr>
<tr>
<td>Ex. 29</td>
<td>1,6-Hexanediame</td>
<td>0.157</td>
<td>93—66°C</td>
<td>60,000 59,000</td>
</tr>
<tr>
<td>25 C. Ex. 10</td>
<td>2-Ethlyhexylamine</td>
<td>0.157</td>
<td>93—66°C</td>
<td>5,200 5,000</td>
</tr>
</tbody>
</table>

While the invention has been described in detail and with respect to specific embodiments thereof, it will be apparent that changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A method of producing a petrolatum or hydrocarbon wax oxidate composition comprising reacting simultaneously or in any order:
   (a) a hydrocarbon wax oxidate, a petrolatum oxidate or a mixture of said hydrocarbon wax oxidate and said petrolatum oxidate, and
   (b) a polyamine having at least two amino groups, each group having at least one active hydrogen atom, characterized in that an amount of from 0.04 to 7% by weight of the polyamine based on the weight of said oxidate is used, whereby a sinewy or film-forming reaction product is obtained.

2. A method of producing a metal salt of a petrolatum or hydrocarbon wax oxidate composition comprising reacting simultaneously or in any order:
   (a) a hydrocarbon wax oxidate, a petrolatum oxidate or a mixture of said hydrocarbon wax oxidate and said petrolatum oxidate;
   (b) a polyamine having at least two amino groups, each group having at least one active hydrogen atom, and
   (c) a metal salt forming compound, characterized in that an amount of the polyamine is used ranging from 0.04 to 7% by weight based on the weight of said oxidate, and an amount of the salt forming compound is used ranging of from 90% to about 150% equivalency based on the acid number of the oxidate composition being prepared, whereby a sinewy or film-forming reaction product is obtained.

3. The method of claim 1 or 2, wherein said oxidate (a) is the oxidation product of a hydrocarbon wax or petrolatum having an acid number ranging from 20 to 150.

4. The method of claim 1 or 2, wherein said polyamine is a diamine, a triamine, a tetramine or a pentamine.

5. The method of claim 1 or 2, wherein said polyamine is an aliphatic polyamine, and alicyclic polyamine, and aromatic polyamine or a heterocyclic polyamine.

6. The method of claim 1 or 2, wherein said polyamine is triethylene tetramine, diethylene triamine, tetraethylenepentamine, hexamethylenediamine, ethylene diamine, or piperazine.

7. The method of claim 1 or 2, wherein said polyamine is triethylene tetramine.

8. The method of claim 1 or 2, wherein said polyamine is a polyfunctional amino group containing nitrogen compounds from hydrogenated coal or shale oil.

9. The method of claim 2, wherein said metal salt is a salt of lithium, sodium, potassium, magnesium, rubidium, strontium, cesium, barium, cadmium, aluminum, tin, bismuth or zinc.
Patentansprüche

1. Verfahren zur Herstellung einer Vaselin- oder Kohlenwasserstoffwachs-Oxidationsmasse, wobei gleichzeitig oder in beliebiger Reihenfolge umgesetzt werden:
(a) ein Kohlenwasserstoffwachs-Oxidationsmittel, ein Vaselin-Oxidationsmittel oder ein Gemisch beider und
(b) ein Polymarin, das wenigstens zwei Aminogruppen aufweist, sowie jede Gruppe wenigstens ein aktives Wasserstoffatom besitzt, dadurch gekennzeichnet, daß eine Menge von 0,04 bis 7 Gew.% des Polyamins auf der Gewichtsgrundlage des Oxidationsmittels angewandt wird, wodurch ein zähes oder filmbildendes Umsetzungsprodukt erhalten wird.

2. Verfahren zum Herstellen eines Metallsalzes eines Vaselin- oder Kohlenwasserstoffwachs-Oxidationsmittels, wobei gleichzeitig oder in beliebiger Reihenfolge umgesetzt werden:
(a) ein Kohlenwasserstoffwachs-Oxidationsmittel, ein Vaselin-Oxidationsmittel oder ein Gemisch beider,
(b) ein Polymarin, das wenigstens zwei Aminogruppen aufweist, wobei jede Gruppe wenigstens ein aktives Wasserstoffatom enthält und
c) eine ein Metallsalz bildende Verbindung, dadurch gekennzeichnet, daß das Polymarin in einer Menge von 0,04 bis 7 Gew.-% bezogen auf das Gewicht des Oxidationsmittels und die salzbildende Verbindung in einer Menge von 90 bis etwa 150% Equivalenten bezogen auf die Säurezahl des Oxidationsmittels angewandt wird, wodurch ein zähes oder filmbildendes Umsetzungsprodukt erhalten wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Oxidationsmittel (a) das Oxidationsprodukt eines Kohlenwasserstoffwachses oder Vaselins mit einer Säurezahl von 20 bis 150 ist.

4. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Polymarin ein aliphatisches Polyamin, allylisches Polyamin, aromatisches Polyamin oder ein heterocyclisches Polyamin ist.

5. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Polyamin ein Diamin, Triamin, Tetramin oder Pentamin ist.


7. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Polyamin Tetraäthylenpentamin ist.

8. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Polyamin eine polyfunktionelle Aminogruppe ist, die Stickstoffverbindungen aus hydrierter Kohle oder Schieferöl enthält.


Revendications

1. Un procédé de production d'une composition d'oxydant de pétrolatum ou de cire hydrocarbonée comprenant le fait de faire réagir simultanément ou dans un ordre quelconque:
   a) un oxydant de cire hydrocarbonée, un oxydant de pétrolatum ou un mélange dudit oxydant de cire hydrocarbonée et dudit oxydant de pétrolatum, et
   b) une polynamine présentant au moins deux groupes amino, chaque groupe présentant au moins un atome d'hydrogène actif, caractérisé en ce qu'on utilise une quantité allant de 0,04 à 7% en poids de la polynamine sur la base du poids dudit oxydant, de sorte que l'on obtient un produit de réaction filamentex ou filmogène.

2. Un procédé de production d'un sel métallique d'une composition d'oxydant de pétrolatum ou de cire hydrocarbonée comprenant le fait de faire réagir simultanément ou dans un ordre quelconque:
   a) un oxydant de cire hydrocarbonée, un oxydant de pétrolatum ou un mélange dudit oxydant de cire hydrocarbonée et dudit oxydant de pétrolatum;
   b) une polynamine présentant au moins deux groupes amino, chaque groupe présentant au moins un atome d'hydrogène actif, et
   c) un composé formant un sel métallique, caractérisé en ce qu'on utilise une quantité de polynamine allant de 0,04 à 7% en poids sur la base de poids dudit oxydant, et en ce qu'on utilise une quantité du composé formant un sel allant de 90% à environ 150% sur la base d'une équivalence de l'indice d'acide de la composition d'oxydant preparée, de sorte que l'on obtient un produit de réaction filamentex ou filmogène.

3. Le procédé de la revendication 1 ou 2, dans lequel ledit oxydant (a) est le produit d'oxygenation d'une cire hydrocarbonée ou d'un pétrolatum présentant un indice d'acide allant de 20 à 150.

4. Le procédé de la revendication 1 ou 2, dans lequel ladite polynamine est une diamine, une triamine, une tétramine ou une pentamine.

5. Le procédé de la revendication 1 ou 2, dans lequel ladite polynamine est une polynamine aliphatique, et une polynamine alycyclique et une polynamine aromatique ou une polynamine hétérocyclique.
6. Le procédé de la revendication 1 ou 2, dans lequel ladite polyamine est la triéthylène tétramine, la diéthylène triamine, le tétraéthylène pentamine, l'héxaméthylène diamine, l'éthylène diamine ou la pipérazine.
7. Le procédé de la revendication 1 ou 2, dans lequel ladite polyamine est la tétraéthylène pentamine.
8. Le procédé de la revendication 1 ou 2, dans lequel ladite polyamine est un groupe amino polyfonctionnel contenant des composés azotés pris parmi le charbon hydrogéné ou l'huile de schiste.
9. Le procédé de la revendication 2, dans lequel ledit sel métallique est un sel de lithium, sodium, potassium, magnésium, rubidium, strontium, césium, baryum, cadmium, aluminium, étain, bismuth ou zinc.