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GREASE COMPOSITION THICKENED WITH A METAL N-SUBSTITUTED CARBAMATE

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This invention relates to new and useful improvements in greases and more particularly to an improved high-temperature grease utilizing metal carbamate salts as thickeners.

Metal soaps, such as sodium, lithium, and calcium soaps of fatty acids are the most widely used gelling agents for thickening lubricating oils to the consistency of a grease. Many of the metal soaps, however, increase the tendency of grease compositions to oxidation and necessitate the use of large amounts of oxidation inhibitors. Most soap-thickened greases also tend to melt at low temperatures, and have a tendency to bleed.

The grease compositions of this invention are more resistant to oxidation than those thickened with metal soaps, are substantially free from bleeding, and have very high dropping points.

It is one object of this invention to provide an improved grease composition which is nonbleeding and has a very high dropping point.

Another object of this invention is to prepare an improved grease composition having improved resistance to oxidation.

A feature of this invention is the provision of improved grease compositions utilizing metal salts of organic-substituted carbamic acids which have high dropping points, low tendency to bleed, and resistance to oxidation.

Other objects and features of this invention will become apparent from time to time throughout the specification and claims as hereinafter related.

This invention is based upon my discovery that greases having high oxidation stability, high dropping point, and low tendency to bleed can be prepared by thickening oleaginous lubricating liquids, such as mineral lubricating oils and synthetic lubricants, with 5 to 30 wt. percent of metal hydrocarbyl-substituted carbamates. The carbamate salts which are useful in the formation of greases in accordance with this invention are of the formula $(RR'NCO_2)_xM$, where R and R' are hydrogen or C_1 - C_{30} hydrocarbyl radicals (at least one being hydrocarbyl), M is a metal of the group consisting of alkali and alkaline earth metals, aluminum, lead, and tin, and x is a subscript corresponding to the valence of M. Examples of these salts include sodium dimethylcarbamate, lithium dimethylcarbamate, potassium dimethylcarbamate, cesium dimethylcarbamate, rubidium dimethylcarbamate, sodium methylcarbamate, sodium butylcarbamate, sodium benzylcarbamate, lithium 1-methyl-octylcarbamate, calcium bis (butylcarbamate), calcium bis (dimethylcarbamate), calcium bis (stearylcarbamate), barium bis (dimethyl carbamate), barium bis (dodecylcarbamate), strontium bis (methylcarbamate), strontium bis (stearylcarbamate), aluminum tris (methylcarbamate), aluminum tris (decylcarbamate), lead (II) bis (dimethylcarbamate), lead (IV) tetrakis (methylcarbamate), tin (II) bis (hexadecylcarbamate), tin (IV) tetrakis (methylcarbamate), and tin (IV) tetrakis (butylcarbamate).

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Lubricant liquids which may be used in this invention include oleaginous lubricating liquids of lubricating viscosity and lubricating properties of all kinds. These liquids include mineral lubricating oils and synthetic organic lubricants, such as polyoxyalkyleneglycols, liquid esters of mono- and di-carboxylic acids, polyesters, esters of polyhydric alcohols, liquid esters of acids of phosphorus and silicon, and polysiloxanes.

In one embodiment, the grease compositions of this invention are prepared by forming a dispersion of molten sodium, lithium, or other metal or other colloidal dispersion of the metal, in the lubricating liquid and reacting the same with a mono- or di-hydrocarbyl amine and carbon dioxide to form the metal hydrocarbyl-substituted carbamate in situ in the lubricating liquid. The reaction mixture sets to a gel-like grease structure as the reaction proceeds. If a softer grease is desired, additional lubricating liquid is added with the amine to cut the mixture back to the desired concentration of the carbamate salt in the lubricant liquid.

In another embodiment, the amine and carbon dioxide are reacted to produce an ammonium salt according to the equation $2RR'NH + CO_2 \rightarrow RR'NCO_2NH_2RR'$, where R and R' are as above-described. This ammonium salt is then reacted with a dispersion of the desired metal (of substantially colloidal size) in oil to displace the amine and hydrogen to form the metal salt of the substituted carbamate. The amine is distilled (or otherwise removed, e.g., by extraction, etc.) from the oil-metal carbamate salt mixture and a gel-like grease structure is obtained.

In still another embodiment, a dispersion of an N-substituted amide of the desired metal is formed in the oil (or other oleaginous liquid) by reaction of an amine with a dispersion of the metal or with a dispersion of the amide of the metal. The resulting N-substituted metal amide is then reacted with carbon dioxide to produce the desired metal N-substituted carbamate in situ, forming a grease-like gel structure.

The following examples illustrate methods of preparing greases which are thickened with alkali-metal, N-substituted carbamates according to this invention.

Example I

A dispersion (25 wt. percent) of 5.2 parts by wt. of sodium and 15.6 parts by wt. of 200 viscosity neutral oil was prepared by heating a mixture of sodium and neutral oil in an atmosphere of nitrogen until the sodium had melted, followed by stirring at high speed until a fine dispersion was effected. The dispersion was then cooled below the melting point of sodium without stirring. To this dispersion of sodium in neutral oil, there were added 10.1 parts by wt. of dimethylamine and 59.2 parts by wt. of 200 viscosity neutral oil. Carbon dioxide was then bubbled into the mixture with stirring, until 9.9 parts by wt. of carbon dioxide had reacted with the sodium dispersion and amine to produce a colloidal dispersion of 25.2 parts of sodium dimethyl carbamate, $(CH_3)_2NCO_2Na$, in 74.8 parts of mineral lubricating oil. After reaction and cooling, a light yellow, buttery grease was formed which had a worked penetration of about 200, had high shear stability and storage stability, was free from bleeding, and had a dropping point in excess of 380° F.

Example II

In another experiment, the method of preparation of Example I was followed except that sufficient oil was added with the amine to produce a grease containing only 18.2 wt. percent of sodium dimethylcarbamate. This grease had an unworked penetration of 338 and a worked penetration of 344. The penetration of the grease increased less than 1 unit after working 1000 strokes in

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an ASTM grease worker using a $\frac{1}{4}$ " hole plate. The unworked penetration of this grease after three months storage was 338. There was no evidence of bleeding upon storage, and the dropping point of the grease was in excess of 380° F.

Example III

The procedure of Example II is duplicated except that a silicone oil (polymethylsiloxane) is substituted for the mineral oil. When the sodium dimethylcarbamate is formed in situ, a grease is obtained.

Example IV

The method of grease preparation of Example II is repeated, substituting tricresylphosphate for the mineral oil. After the formation of sodium dimethylcarbamate in the liquid is complete, a grease is obtained.

Example V

The method of preparation of Example II is repeated, substituting diisooctylazolate for the mineral oil. As the sodium dimethylcarbamate is formed in situ, a grease is obtained.

Example VI

A dispersion of 2.1 parts sodium in 6.3 parts of 200 viscosity neutral oil was formed following the procedure of Example I. To this dispersion, there were added 9.1 parts of hexylamine and sufficient mineral oil to bring the total amount of oil to 84.9 parts. Carbon dioxide was then bubbled through the mixture until 3.9 parts had reacted with the sodium and amine to form sodium hexylcarbamate, $C_6H_{13}NHCO_2Na$, in a concentration of 15.1 wt. percent. A clear grease was formed. This grease had a worked penetration of 270 and increased in penetration by 53 units upon working 1000 strokes in an ASTM grease worker using a $\frac{1}{4}$ " hole plate. This grease had an unworked penetration of 198 after 3 months' storage, exhibited no bleeding, and had a dropping point of 380° F.

Example VII

A dispersion of 2.5 parts of sodium in 7.5 parts of 200 viscosity mineral oil was formed, following the procedure of Example I. To this dispersion there were added 7.9 parts of n-butylamine and 77.4 parts of 200 viscosity mineral oil, thus producing a dispersion of sodium N-n-butylamide. Carbon dioxide was then bubbled through the dispersion until 4.7 parts had reacted with the sodium N-n-butylamide to form sodium n-butylcarbamate in a 15.1 wt. percent concentration. A clear, light yellow grease was formed. This grease had a worked penetration of 269 and increased in penetration by 45 units after working 1000 strokes in an ASTM grease worker using a $\frac{1}{4}$ " hole plate. This grease had an unworked penetration of 193 after 3 months' storage, exhibited no tendency to bleed, and had a dropping point of 384° F.

Example VIII

A dispersion of 51.8 parts of sodium in 200 vis. neutral oil was formed following the procedure of Example I. To this dispersion, there was added 301.9 g. of dimethylammonium dimethylcarbamate (formed by the in situ reaction of dimethylamine and carbon dioxide) in a liquid mixture consisting of 462 g. of 200 vis. neutral oil and 800 g. of tetrahydrofuran. When the reaction was complete, dimethylamine (released during the reaction) and tetrahydrofuran were distilled from the mixture, leaving a clear, buttery, tough grease, containing 25 wt. percent sodium dimethylcarbamate.

This grease was cut back with 375 g. of 200 vis. neutral oil to 18 wt. percent sodium dimethylcarbamate. The final grease was clear (almost transparent), appeared to undergo little or no change in consistency when heated to 330° F. with agitation, and did not bleed upon standing for two days after being cooled to room temperature. This grease had an unworked penetration of 338

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and a worked penetration of 344. After being milled at 0.003" clearance, the grease had a worked penetration of 352 and a penetration of 354 after 5000 strokes. The dropping point was in excess of 380° F. This grease is useful as a high-temperature bearing grease.

Example IX

In another experiment 172 g. of n-hexylamine were added to 1182 g. of 200 vis. neutral oil in a 5-pound, covered grease kettle, with stirring. An excess of carbon dioxide was passed through the stirred mixture to form N-n-hexylammonium N-n-hexylcarbamate in an exothermic reaction (the mixture increased in temperature to 50° C.). The oil was gelled by the ammonium salt which was formed therein. To this grease there was added 31 g. of sodium dispersed in 93 g. of mineral lubricating oil. The grease first appeared to get softer, but as the reaction with sodium progressed (evidenced by gradual fading of the grey color of unreacted sodium), the grease became tougher and clear. Additional carbon dioxide was passed through the mixture to assure complete reaction of the ammonium salt with the metal present. The resultant clear grease was heated to 300° F. to distill off the unreacted amine and was cooled to room temperature with agitation.

The grease had a worked penetration of 220, was non-bleeding, and had a dropping point in excess of 380° F.

Example X

A dispersion of lithium in 200 viscosity neutral oil is prepared by heating a mixture of 1.4 parts by wt. lithium and 7 parts by wt. oil in an atmosphere of nitrogen to a temperature of about 400° F., then stirring at high speed until a fine dispersion of molten lithium is effected. The dispersion is then cooled below the melting point of lithium without stirring. To this dispersion, there are added 9.0 parts by wt. dimethylamine and 74 parts by wt. of 200 viscosity neutral oil. Carbon dioxide is then bubbled through this mixture until 8.8 parts by wt. have reacted with the dispersed lithium and amine to form in situ lithium dimethylcarbamate in a concentration of 19 wt. percent. As this reaction progresses, a grease is formed which has no tendency to bleed and which has a dropping point in excess of 400° F.

Example XI

When the procedure of Example I is repeated substituting sodium-potassium alloy, containing 56 wt. percent potassium, for the sodium, the mineral oil dispersion is formed and heated to about 200° F. The reaction with dimethylamine and carbon dioxide produces a mixture of sodium dimethylcarbamate and potassium dimethylcarbamate which sets into a grease. A potassium dimethylcarbamate grease may be prepared in the same manner using a dispersion of potassium metal in mineral oil.

Example XII

In another experiment, 42.6 g. (0.152 mol) of Armeen 18 D (product of Armour and Co.), 1.05 g. (0.152 mol) of lithium metal, and 150 g. of 200 vis. neutral oil were charged to a 500 ml., creased flask equipped with a high-speed stirrer and heated to 365° F. with moderate stirring. Armeen 18 D is primary fatty amine of the formula RNH_2 , where the R groups consists of approximately 6% C_{16} saturated alkyl radicals, 93% C_{18} saturated alkyl radicals, and 1% C_{18} alkenyl radicals. It was noted that the surfaces of the metal particles became bright at about 210°–250° F. indicating reaction. Agitation was slowly increased, and the mixture in the flask assumed a dark, brownish-red color. Lithium metal appeared to be reacting and all of the metal was dissolved or reacted before maximum agitation was attained. A gas (hydrogen) was given off as evidenced by escape from foam. The reaction was exothermic and reached a maximum temperature of 400° F. No lithium

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particles were present and no settling of the dispersion occurred when the solution was cooled. This is in marked contrast to the preparation of lithium dispersions in an unreactive medium, wherein maximum agitation for at least 10 minutes is required and particles of metal begin to rise to the surface within a few minutes after stirring is stopped. Satisfactory lithium dispersions cannot ordinarily be effected in glassware due to an exothermic reaction between the lithium metal and the glass above the melting point of the metal. The product of the above reaction is a lithium N-substituted amide of the formula LiNHR , where R is as above defined.

The oil dispersion of lithium N-substituted amide produced above was reacted with an excess of carbon dioxide to form in situ the lithium N-substituted carbamate of the formula RHNCO_2Li , where R is derived from the fatty amine and is of the composition described above. The oil containing 25 wt. percent of the lithium N-substituted carbamate salt was cooled and formed a tough, NLGI No. 2 grade grease. This grease was water resistant, had a high melting point, and contained no unreacted lithium.

Example XIII

In still another experiment, a grease was prepared using the lithium salt of 1-methyl-octyl carbamic acid. A 29.6 g. (0.207 mol) portion of 1-methyl-octyl amine, 1.44 g. of lithium metal (0.207 mol) and 160 g. of 200 vis. neutral oil were charged to a 500 ml., creased flask, equipped with a high-speed stirrer, as in Example XII. Again, the dark, brownish-red color developed and all of the metal appeared to have been consumed by reaction before maximum agitation was achieved, at $365^\circ\text{--}375^\circ\text{F}$. An excess of carbon dioxide gas was passed through the flask at 265°F . An exothermic reaction between the carbon dioxide and the lithium 1-methyl-octyl amide raised the temperature to 285°F ., and the mixture gelled as the color disappeared. The resultant grease contained 20 wt. percent of the lithium 1-methyl-octyl carbamate, was a clear amber color, and had the consistency of an NLGI No. 1 grade grease. The grease was water resistant and had a very high melting point, but appeared to have a small amount of unreacted lithium present as indicated by effervescence with water. When the grease was treated with water to remove the unreacted lithium, the resultant grease had a translucent amber color and the consistency of an NLGI No. 2 grade grease after removal of the water.

A second batch of this grease was prepared as above, except that 15 wt. percent of the salt was employed to gel the oil, and stirring was continued at 400°F . for a slightly longer period of time. A small sample of the grease, after reaction of the metal N-substituted amide with carbon dioxide, was removed and treated with water and found to contain unreacted lithium. The grease was heated, with stirring, to 375°F ., at which temperature unreacted amine appeared to be distilling. Ten percent excess amine was added and heating continued for about 10 minutes. The grease became more fluid and somewhat grainy. It was cooled to room temperature and was semifluid. A sample was worked with a spatula to eliminate most of the graininess and convert the mixture into a grease having a consistency intermediate that of NLGI No. 1 and No. 2 grade greases.

Still another sample of this grease was diluted with hexane and stirred to produce a mixture containing 2.5 wt. percent of the lithium N-substituted carbamate salt. The mixture became a clear, translucent, No. 0 grade grease and had no unreacted lithium present. Evaporation of the hexane resulted in a smooth No. 2 grade grease which was water resistant and highly stable to shear. A sample of this grease did not melt at the flash point of the oil (approximately 400°F .) nor while the oil was burning. This is an extremely unusual property for a grease thickened with an organic compound, and is

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usually evidenced only by greases containing inorganic thickeners such as silica and bentonite.

Example XIV

Still another grease was prepared using the procedure of Example XII with a lithium dispersion and Armeen C (product of Armour and Co.) as the reactants. Armeen C is a primary amine of the formula RNH_2 , where R is a mixture of hydrocarbyl radicals derived from coconut oil and consists of approximately 8% C_8 , 9% C_{10} , 47% C_{12} , 18% C_{14} , 8% C_{16} , and 5% C_{18} , saturated, and 5% C_{18} , unsaturated, hydrocarbon radicals. Upon carbonation of the dispersion of lithium N-substituted amides, the reddish color was discharged rapidly, and a soft, greenish-gray, grease resulted. The grease contained 15 wt. percent of the lithium N-substituted carbamate gelling agent. Upon standing for 4 hours at room temperature, the grease became firmer and was very smooth.

Example XV

In still another embodiment of this invention, a lithium butyl carbamate grease is prepared at a 15 wt. percent salt concentration by reacting 4.9 g. of lithium amide (LiNH_2) with 15.6 g. of n-butyl amine, and carbon dioxide in 170 g. of 200 vis. neutral mineral oil. The lithium amide (0.214 mol) is first dispersed in the mineral oil and n-butyl amine (0.214 mol) is reacted therewith to evolve ammonia and convert the lithium amide to a lithium N-substituted amide, according to the equation $\text{LiNH}_2 + \text{C}_4\text{H}_9\text{NH}_2 \rightarrow \text{LiHNC}_4\text{H}_9 + \text{NH}_3\uparrow$. When ammonia evolution stops, the flask is swept free of ammonia by passing nitrogen therethrough. Carbon dioxide is then passed through the flask, with stirring, as in the previous examples. An exothermic reaction occurs to form lithium butyl carbamate and the mixture gels as the reaction nears completion. The grease which is thus produced has a consistency of about an NLGI No. 1 grade grease, is non-bleeding, and is water resistant.

Example XVI

A calcium bis (butyl carbamate) grease, containing 15 wt. percent of the carbamate salt, is made following the procedure of Example XV. Calcium amide, prepared by high temperature reaction of finely-divided calcium metal and ammonia, is dispersed in 200 vis. neutral mineral oil and reacted with n-butyl amine to displace the ammonia and form calcium bis n-butyl amide. The calcium N-substituted amide is then reacted with carbon dioxide, with stirring, to produce in an exothermic reaction the desired calcium N-substituted carbamate salt. The mixture gels to a semifluid condition corresponding to an NLGI No. 00 grade grease. When the concentration of the calcium N-substituted carbamate in the grease is increased to about 25 wt. percent, an NLGI No. 1 grade grease is obtained. When Armeen 18 D is substituted for the n-butyl amine in this process, a calcium bis (alkyl carbamate) is formed in which the alkyl groups are derived from the mixture of fatty amines used. A clear, water-resistant grease is obtained.

Example XVII

A magnesium bis (methyl carbamate) grease, containing 15 wt. percent of the carbamate salt, is made following the procedure of Example XV by reacting finely-divided magnesium with methylamine and carbon dioxide to produce the desired magnesium N-substituted carbamate. The reaction is exothermic and upon completion of reaction, the mixture sets into a grease.

Example XVIII

A saturated solution of barium metal in liquid ammonia at room temperature is prepared in an autoclave by charging finely-divided barium metal, liquid ammonia, and 200 vis. neutral lubricating oil. The autoclave is agitated to form an ammonia solution of barium metal

which is thoroughly mixed with the lubricating oil. Thereupon the ammonia pressure is released. Upon release of pressure, the ammonia evaporates from the autoclave and leaves the barium metal dispersed in the mineral oil in particles of colloidal size. The colloidal dispersion of barium is flushed with nitrogen to remove any ammonia remaining in solution. To this dispersion of barium in mineral oil, there is added dimethylamine and carbon dioxide, with agitation. An exothermic reaction results which produces barium bis (dimethyl carbamate) and causes the mineral oil to gel into a firm grease.

Example XIX

An aluminum sol in 200 vis. neutral lubricating oil is prepared by the Bredig-Svedberg method. A high-frequency electric arc is struck between a pair of aluminum electrodes and the arc is swept by a stream of nitrogen into a beaker of 200 vis. neutral lubricating oil. The vaporized aluminum from the arc is condensed in the mineral oil and forms a sol containing aluminum particles of colloidal size. Dimethyl ammonium dimethylcarbamate prepared in accordance with Example VIII is added to the aluminum sol and heated to 250° F. with agitation. After the reaction is complete, as evidenced by the subsidence of hydrogen evolution, the mixture is heated to expel by-product dimethylamine and then cooled. There is obtained a tough, clear grease as a result of gelling by the aluminum tris (dimethylcarbamate) produced by the reaction.

Example XX

A lead dispersion in mineral lubricating oil is prepared as described in Example XIX, by the Bredig-Svedberg method. This dispersion is mixed with n-butyl amine and agitated while being heated to 250° F. Carbon dioxide is bubbled through the reaction mixture to produce a dispersion of lead bis (butylcarbamate) which sets into a grease upon completion of the reaction.

Example XXI

A dispersion of tin in mineral lubricating oil is prepared by the Bredig-Svedberg method as described in Example XIX. This dispersion is reacted with diethylamine and carbon dioxide at 300° F. with agitation. The reaction which takes place in exothermic and produces a fine dispersion and partial solution of tin (II) bis (diethylcarbamate) which sets into a gel on completion of reaction.

While I have described my invention fully and completely, as required by the patent laws, with special emphasis upon several preferred embodiments of this invention, I wish it understood that within the scope of the appended claims, this invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A grease composition consisting essentially of an oleaginous lubricating liquid of lubricating viscosity and a minor amount, sufficient to gel the liquid, of a metal N-substituted carbamate of the formula $M(NR_2CO_2)_x$, where M is selected from the group consisting of alkali metals, alkaline earth metals, aluminum, tin, and lead, x is the valence of M, and R is of the group consisting of hydrogen and C_1-C_{30} alkyl and aralkyl radicals, at least one R being a C_1-C_{30} radical.

2. A grease composition according to claim 1 in which the metal N-substituted carbamate is present in a concentration of about 5-30 wt. percent.

3. A grease composition in accordance with claim 2 in which M is an alkali metal.

4. A grease composition in accordance with claim 2 in which M is an alkaline earth metal.

5. A grease composition according to claim 2 in which M is sodium.

6. A grease composition according to claim 2 in which M is lithium.

7. A grease composition according to claim 2 in which R is a lower alkyl radical.

8. A grease composition according to claim 2 in which the oleaginous liquid is of the group consisting of mineral lubricating oils and synthetic organic lubricants.

9. A grease composition consisting essentially of a mineral oil of lubricating viscosity and a minor amount, in the range of about 5-30%, sufficient to gel the oil, of an alkali metal N-substituted carbamate of the formula MNR_2CO_2 , where M is an alkali metal, and R is of the group consisting of hydrogen and C_1-C_{30} alkyl and aralkyl radicals, at least one R being a C_1-C_{30} radical.

10. A grease composition consisting essentially of a mineral oil of lubricating viscosity and a minor amount, in the range of about 5-30%, sufficient to gel the oil, of an alkali metal N-substituted carbamate of the formula $M(NR_2CO_2)_2$, where M is an alkaline earth metal, and R is of the group consisting of hydrogen and C_1-C_{30} alkyl and aralkyl radicals, at least one R being a C_1-C_{30} radical.

11. A grease composition according to claim 9 in which the alkali metal N-substituted carbamate is sodium dimethylcarbamate.

12. A grease composition according to claim 9 in which the alkali metal N-substituted carbamate is sodium butylcarbamate.

13. A grease composition according to claim 9 in which the alkali metal N-substituted carbamate is sodium hexylcarbamate.

14. A grease composition according to claim 9 in which the alkali metal N-substituted carbamate is sodium benzylcarbamate.

15. A grease composition in accordance with claim 9 in which the alkali metal N-substituted carbamate is sodium stearylcarbamate.

16. A grease composition according to claim 9 in which the alkali metal N-substituted carbamate is lithium dimethylcarbamate.

17. A grease composition according to claim 9 in which the alkali metal N-substituted carbamate is a mixture of sodium and potassium dimethylcarbamates.

18. A grease composition according to claim 10 in which the carbamate used is a barium N-substituted carbamate.

19. A grease composition according to claim 10 in which the carbamate used is a magnesium N-substituted carbamate.

20. A grease composition according to claim 10 in which the carbamate used is a calcium N-substituted carbamate.

21. A method of preparing a metal N-substituted carbamate-thickened grease which comprises reacting a dispersion of a finely-divided metal of the group consisting of alkali and alkaline earth metals, aluminum, tin, and lead, in an oleaginous lubricating liquid of lubricating viscosity with sufficient CO_2 and R_2NH , where R is of the group consisting of hydrogen and C_1-C_{30} alkyl and aralkyl radicals, at least one R being a C_1-C_{30} radical, to form a metal N-substituted carbamate salt in situ and produce a grease.

22. A method of preparing a metal N-substituted carbamate-thickened grease which comprises reacting a dispersion of a metal of the group consisting of alkali and alkaline earth metals, aluminum, tin, and lead, in an oleaginous lubricating liquid of lubricating viscosity, with an alkyl ammonium alkyl carbamate of the formula $R_2NH_2CO_2NR_2'$, where R and R' are of the group consisting of C_1-C_{30} alkyl and aralkyl radicals and hydrogen, at least one R being a C_1-C_{30} radical, and separating the by-product amine to produce a grease.

23. A method of preparing a metal N-substituted carbamate-thickened grease which comprises reacting a dispersion of a metal N-substituted amide of the formula $M(NR_2)_x$, where M is of the group consisting of alkali and alkaline earth metals, aluminum, tin and lead, R is

of the group consisting of hydrogen and C_1-C_{30} alkyl and aralkyl radicals, at least one R being a C_1-C_{30} radical, and x is an integer corresponding to the valence of M, with carbon dioxide to form in situ an N-substituted carbamate of the formula $M(CO_2NR_2)_x$, where M, R and x are as above-defined, and produce a grease.

24. A method according to claim 23 in which the metal N-substituted amide is produced in situ by reaction

of a dispersion of the metal M with an amine of the formula, R_2NH , where R and M are as above defined.

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