US 20060019842A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2006/0019842 A1**

Finmans et al. (43) **Pub. Date: Jan. 26, 2006**

(54) **ALUMINUM COMPLEX GREASE**

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(21) Appl. No.: **11/214,649**

(22) Filed: **Aug. 30, 2005**

Related U.S. Application Data

(62) Division of application No. 10/221,336, filed on Feb. 3, 2003, filed as 371 of international application No. PCT/DE01/00829, filed on Mar. 6, 2001.

(30) **Foreign Application Priority Data**

Mar. 10, 2000 (DE)..... 10011333.8

Publication Classification

(51) **Int. Cl.**
C10M 117/00 (2006.01)

(52) **U.S. Cl.** **508/525**; 508/537

(57) **ABSTRACT**

This invention relates to a thickener component based on an aluminium carboxylate compound and to an aluminium complex grease made therefrom with addition of a base liquid.

ALUMINUM COMPLEX GREASE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a divisional of U.S. patent application Ser. No. 10/221,336 filed on Feb. 03, 2003, for Thickener Component and Aluminum Complex Grease, the disclosure of which is incorporated herein by reference.

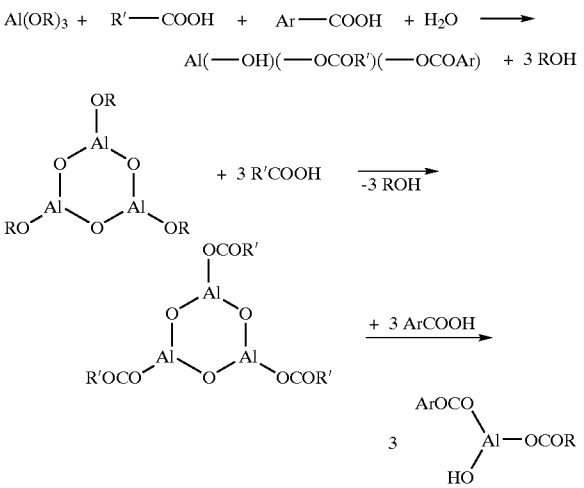
BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] This invention relates to a thickener component based on an aluminium carboxylate compound and to an aluminium complex grease made therefrom with addition of a base liquid.

[0004] 2. Description of the Prior Art

[0005] Aluminium complex greases have been known. They essentially comprise a mineral-oil base liquid and a thickener system containing one or more aluminium carboxylate compounds. The aluminium carboxylate compound is obtained by reacting a fatty acid and/or an aromatic carboxylic acid with an aluminium alcoholate derivative. The industrially used aluminium alcoholates comprise aluminium isopropoxylate and tri-oxy-aluminium-triisopropoxide. In theory, the reaction proceeds as shown hereinbelow:



[0006] When using aluminium isopropoxylate, partial hydrolysis is performed with water before, during, or after reaction of the acids with aluminium alcoholate to produce the usually required free -OH group on the aluminium. Aluminium complex greases are distinguished by a high dropping point, good conveyance and water resistance, and low separation of oil.

SUMMARY OF THE INVENTION

[0007] It is an object of this invention to provide more effective aluminium complex greases, in particular more suitable thickener components for manufacturing thickeners for aluminium complex greases. The term 'more effective' shall mean that the grease exhibits better lubricating properties than conventional aluminium complex greases. Furthermore, it is desired that the thickener component employed for making said aluminium complex greases be storable and marketable as such, thus enabling the grease manufacturer to produce the thickener-containing grease himself.

[0008] According to this invention, the problem has been resolved by providing a thickener component comprising

[0009] (A) from 99.99 to 94 weight percent, preferably 99.9 to 97 weight percent of an aluminium compound which can be prepared by reacting a hydrolysable aluminium compound with one or more aliphatic monocarboxylic acid(s) or aliphatic derivatives thereof, optionally in the presence of water and/or a C_1- to C_{40}-alcohol, thereby forming one or more aluminium compound(s) having at least one aluminium carboxylate bond per aluminium atom and, in addition, one or more aluminium-, hydroxy-, aluminium alcoholate-, and/or aluminium-oxygen-aluminium bond(s) and

[0010] (B) from 0.01 to 6 weight percent, preferably 0.1 to 3 weight percent of an ester compound having from 6 to 60 carbon atoms,

each referring to the total of components (A) and (B).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] The term 'hydrolysable aluminium compounds' as used herein refers to aluminium compounds that are capable of forming aluminium-oxygen bonds by the action of protondonating compounds, such as water or organic acids. Preferably, such hydrolysable aluminium compounds are aluminium alcoholate- or aluminium-oxo-alcoholate compounds with the alcoholate group preferably being a C_2- to C_4-alcohol, particularly isopropanolate. The carboxylic acids can be branched or unbranched aliphatic monocarboxylic acids of the type R^1—COOH, wherein R^1 represents a C_{10}- to C_{40}-radical, preferably a C_{14}- to C_{24}-radical, or a C_{16}- to C_{24}-radical.

[0012] Carboxylic acid derivatives as used herein are defined as compounds which are capable of forming in combination with said aluminium compounds the aluminium-carboxylate bonds that would likewise be obtained when using the corresponding acids. Examples thereof include the anhydrides, acid chlorides, or amides of the aforesaid carboxylic acids.

[0013] Ester compounds as used herein particularly refer to compounds which may be formed by reaction of the alcohols/alcoholates present in the reaction mixture with the carboxylic acids/carboxylate residues.

[0014] The thickener component is prepared by reaction, preferably about equimolar reaction, i.e. about 1 mole of monocarboxylic acid per mole of aluminium atoms in the compound, of a hydrolysable aluminium compound with one or more of the abovementioned carboxylic acid(s) or carboxylic acid derivative(s) at a temperature not exceeding 145° C., most preferably 135° C., with a temperature profile most preferably increasing gradually by at least 20° C. during a period of at least 90 minutes being ensured. It is preferred that the hydrolysable aluminium compound be placed in the vessel first.

[0015] Moreover, it is preferred that the reaction be carried out in a base liquid and the volatile compound released during the reaction, e.g. alcohol, be withdrawn from the equilibrium.

[0016] The term 'thickener' as used herein is defined as a compound or mixture of compounds prepared from the thickener component, which thickener can be produced by reacting the thickener component with aromatic or cyclic monocarboxylic acids of the type R^2—COOH, wherein R^2 represents a C_6- to C_{16}-radical, or with the derivatives thereof. Said (aromatic or cyclic) carboxylic acid derivatives are defined as described hereinabove.

[0017] The resultant aluminium compound preferably has more than 40 mole % of aliphatic monocarboxylic acid radicals, referring to the amount of carboxylate groups (100 mole %=all the carboxylate groups). The remainder is comprised of aromatic or cyclic monocarboxylic acid radicals. As used herein, the term 'aromatic monocarboxylic acid' is defined as a carboxylic acid which has at least one benzene ring or condensed benzene ring and, in addition, may comprise aliphatic hydrocarbon radicals as well. Hence, compounds such as C_6H_5—CH_2—CH_2—. COOH or CH_3—CH_2—C_6H_4—COOH are explicitly included herein.

[0018] The thickener as a constituent of the aluminium complex grease is produced by compounding the thickener component, optionally taken up in additional base liquid, with the aromatic or cyclic monocarboxylic acid.

[0019] The production process of the invention 'yields a raw material (thickener component) with a low ester content for making the real thickener that keeps its low ester content even upon storage.

[0020] Besides the thickeners of the invention the aluminium complex greases of the invention also comprise a base liquid which is a hydrocarbon compound and/or a synthetic oil added to the overall composition in quantities of from 30 to 98 weight percent, preferably 60 to 95 weight percent.

[0021] The hydrocarbon compound can be a paraffin-base or naphthenic mineral oil, a polyalphaolefin, or a white oil. Further synthetic oils which are suitable as base liquid include fatty acid esters based on mono- or multifunctional fatty acids having a chain length of from 8 to 24 carbon atoms and mono- or polyhydric alcohols. Additional constituents of the aluminium complex greases of the invention may be typical additives. Table 1 presents examples of suitable additives.

[0022] The thickener components of the invention are useful as raw materials for producing thickeners included in aluminium complex greases exhibiting improved lubricating properties. They are preferably employed in high-temperature applications for which high dropping points are especially desirable, in central lubricators, and/or for lubricating machinery used for example for producing or processing foodstuffs.

[0023] The prior art thickeners based on aluminium carboxylate compounds or the aluminium complex greases made therefrom have significantly higher ester concentrations. Surprisingly, compositions with lower ester concentrations, preferably less than 6 % in the thickener component, and improved lubricating properties have now become accessible by the process.

[0024] It is preferred that the thickener components as well contain 20 to 80 weight percent, most preferably 30 to 70 weight percent of the base liquid described hereinabove.

Examples of Tests

[0025] Table 2 shows the rheometric values (Physica UDS 200, oscillating measurement, deformation=0.2%, frequency=0.1 Hz, temperature 20° C., plate/plate distance=1 mm) of aluminium complex greases of the invention. Example 4 presents a high ester concentration, whereas the ester concentration in Example 5 (comparative example) is too high. The measurements were made on a thickener component having an aluminium content of 4.1 weight percent. The solvent in the aluminium-containing thickener component is identical with the base oil. The starting material is aluminium isopropanolate. The aliphatic monocarboxylic acid employed herein is a technical-grade stearic acid mixture.

Exemplary Synthesis

[0026] Into a 5-litre agitated vessel equipped with a nitrogen supply line, a 30-cm column (metalized, packed with Raschig rings), and a reflux condenser there are placed 1.466 moles (299.5 g) of DOROX® D 10 (aluminium triisopropylate, liquid) and 500.0 g of Sera® 100 mineral oil (approx. 50 wt. % paraffin-base oil). The educts are heated to 97° C. (bottom temperature) while stirring. The stearic acid is heated to 75-80° C. to keep the product liquid upon feeding. 1.466 moles (393.5 g) of the liquid stearic acid (acid number=209 mg of KOH/g) and the mixture of water (1.372 moles=24.7 g) and 2-propanol (123.6 g) are charged steadily and simultaneously through separate submerged pipes during a period of 2.5 hours. The released 2-propanol is removed overhead (head temperature max. 85° C.). The bottom temperature is gradually increased to 127° C. during this period. Once the bottom temperature reaches 127° C., the pressure is reduced to 200 hPa during 20 minutes and the remainder of the low-boiling 2-propanol is drawn off. During the reaction a distillate comprised of 3.623 moles (217.7 g) of 2-propanol is removed from the reaction and the mixture (123.6 g). The product, oxo-aluminium-stearate, is obtained after purification and filtration. The total residence time of the product at 127° C. is 30 minutes (until end of vacuum phase). Filtration is performed at approx. 120° C. using a 60-μm sieve.

[0027] The material parameters of the thickener component have been compiled in Table 3.

TABLE 1

	Concentration Range, wt. %	
Extreme-pressure additives	2–10	dibenzyldisulfide with chlorinated paraffins; sulphurized fatty oils or terpenes
Additives for enhancing film resistance	0.1–5	diisopropyl- or dilauryl hydrogen phosphite
Rust-inhibiting additives	0.5–5	sodium petroleum sulfonates or barium dinonyl naphthalene sulfonate
Copper deactivators	0.05–1	2-mercaptobenzthiazol
Viscosity index improvers	0.1–1	polymethacrylates
Desludgers	0.001	silicone oils
Additives for producing ropiness	0.5–2	polymers
Antiwear additives	0.1–2	tricresylic phosphate, zinc dialkyl dithiophosphate
Additives for producing water resistance	0.1–2	oil- or other vegetable fatty acids
Deodorants	0.05–0.5	perfumes
Anticorrosion additives	0.5–3	nonylphenoxy vinegar,

TABLE 1-continued

	Concentration Range, wt. %	
		ethylenediamine sulfonate, lead dinonylnaphthyl sulfonate, barium sulfonates, lead- and zinc naphthenates
Oxidation inhibitors		diphenylamine, phenyl-α-naphthylamine, di-octyldiphenylamine, phenothiazine, polymeric trimethyldihydroquinoline, 2,6-di-tert-butyl-4-methylphenol, lead diamyldithiocarbamate, dilaurylthiodipropionate-1/citric acid, ascorbic acid

[0028]

TABLE 2

No.	Base Liquid	Base Liquid Viscosity at 40° C. mm^2/s	Base Liquid Concentration in Grease wt. %	Ester Concentration in Thickener Component wt. %	Base Liquid Concentration in Thickener Component wt. %	Thickener Component Concentration in Grease wt. %	Benzoic Acid Concentration in Grease wt. %	Modulus of Elasticity Pa	Modulus of Viscosity Pa
1	Paraffin-based mineral oil	100	91.3	1.4	60	7.3	1.4	860	330
2	Paraffin-based mineral oil	100	87.1	1.4	60	10.9	2.0	5,720	1,030
3	Paraffin-based mineral oil	100	82.8	1.4	60	14.5	2.7	35,100	5,400
4	Paraffin-based mineral oil	100	87.1	3.9	60	10.9	2.0	1,100	270
5	Paraffin-based mineral oil	100	87.1	8.7	60	10.9	2.0	800	170
6	Naphthene-based mineral oil	100	87.1	1.2	50	10.9	2.0	5,820	1,000
7	Naphthene-based mineral oil	40	87.1	1.2	50	10.9	2.0	2,680	450
8	Polyalpha-olefin	30	91.3	2.4	60	7.3	1.4	290	60
9	Polyalpha-olefin	30	87.1	2.4	60	10.9	2.0	2,100	290
10	Polyalpha-olefin	30	82.8	2.4	60	14.5	2.7	13,300	1,100

[0029]

TABLE 3

		Method
Al content	4.1%	M 635
Turbidity	20 FNU	DIN 38404 T2
Viscosity(25° C.)	1,500 mPa · s	DIN 53015
Viscosity (100° C.)	100 mPa · s	Rotation ($200s^{-1}$)
Pour point	16° C.	DIN ISO 3016

TABLE 3-continued

		Method
2-Propanol concentration	3.5%	
Density (20° C.)	0.94 g/cm^3	DIN 51757
Density (40° C.)	0.93 g/cm^3	DIN 51757
Density (50° C.)	0.93 g/cm^3	DIN 51757
Flash point	190° C.	DIN 51758
Colour number	10	DIN 6162

1-8. (canceled)

9. An aluminum complex grease comprising

a compound or compound mixture obtainable by reacting an ester thickener component with at least one aromatic and/or cyclic monocarboxylic acid, of the type R^1—COOH, wherein R^1 is a C_6 to C_{16} organic moiety, and/or their derivatives and

a base liquid selected from the group consisting of hydrocarbon compounds, synthetic oils and mixtures thereof, said base liquid being present in the grease in an amount of from 30 to 98 weight percent

wherein the thickener component comprises

(A) from 99.99 to 94 weight percent of an aluminum compound obtainable by an approximately equimolar reaction of a hydrolysable aluminum compound with at least one aliphatic monocarboxylic acid or derivatives thereof, in the presence of water and a C_1- to C_{40}-alcohol to form one or more aluminum compound(s) having on average one aluminum carboxylate bond per aluminum atom and, in addition, one or more alumi-

num-hydroxy, aluminum-alcoholate, or aluminum-oxygen-aluminum bond(s) and

(B) from 0.01 to 6 weight percent of an ester compound having from 6 to 60 carbon atoms,

the weight percentage referring to the total of components (A) and (B).

10. An aluminum complex grease of claim 9, characterized in that the hydrolysable aluminum compound is an aluminum-alcoholate or aluminum-oxo-alcoholate compound.

11. An aluminum complex grease according to claim 9, characterized in that the base liquid has a viscosity of from 20 to 200 mm^2/s at 40° C. measured in accordance with DIN 51562.

12. An aluminum complex grease according to claim 9, characterized in that the base liquid is a mineral oil with a boiling point of greater than 250° C.

13. An aluminum complex grease according to claim 9, wherein the base liquid is present in an amount of from 60 to 95 weight percent.

14. An aluminum complex grease according to claim 9, characterized in that said aliphatic monocarboxylic acid is selected from the group consisting of branched or unbranched aliphatic monocarboxylic acids of the type R^2—COOH, wherein R^2 is a C_{10}- to C_{40}-radical, or a derivative thereof.

15. An aluminum complex grease according to claim 14, wherein said R^2 is a C_{14}- to C_{24}-radical.

16. An aluminum complex grease according to claim 9, characterized in that a temperature of 145° C. is not exceeded during the preparation of the aluminum thickener compound by reacting said hydrolysable aluminum compound with said carboxylic acid or said carboxylic acid derivative.

17. An aluminum complex grease of claim 16, wherein the temperature does not exceeded 135° C.

18. An aluminum complex grease according to any one of claims **16** and **17**, characterized in that an increasing temperature profile presenting a temperature difference of at least 20° C. is maintained at a time interval of at least 90 min during the reaction.

19. An aluminum complex grease according to claim 9, wherein the aluminium compound/compound mixture of the aluminum complex grease obtained has more than 40 mol % of aliphatic monocarboxylic acid radicals, referring to the amount of carboxylate groups, the reminder being aromatic and/or cyclic monocarboxylic acid radicals.

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