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IMPROVED OVERBASED CARBOXYLATES

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(56) Prior Art Documents
EP 248465
EP 234149
US 2865956

(57) Claim

1. A process for the production of basic calcium carboxylic acid salts free from mineral oil and catalysts.

i) Neutralising a C_7 to C_{15} aliphatic carboxylic acid in the presence of a volatile solvent.

ii) Adding excess calcium.

iii) Carbonating the mixture at a temperature of from 15°C to 60°C.

iv) Removal of the volatile solvent and water and adding a diluent wherein the carboxylic acid comprises saturated C_8, C_9 and C_{10} oxo acids in which the oxo acids contain less than or equal to 10% by weight of acids which are branched on carbon 2, and greater than 80% by weight of acids which are mono- or polysubstituted on carbon 3 and/or carbons of higher rank, or C_7 to C_{15} acids comprising acids mono- or polysubstituted in the 3- position and/or carbons of higher rank with less from 40% by weight of linear acids and less than 20% by weight of acids substituted on carbon 2.

.../2

8. An overbased calcium carboxylic acid salt, free from mineral oil and catalysts, having a basicity from 4 to 8, in which the carboxylic acid comprises a saturated C_8, C_9 and C_{10} oxo acid in which the oxo acid contains less than or equal to 10% by weight of linear acid, less than or equal to 10% by weight of acids which are branched on carbon 2, and greater than 80% by weight of acids which are mono- or polysubstituted in the 3- position and/or carbons of higher rank, with less than 40% by weight of linear acids and less than 20% by weight of acids substituted on carbon 2.

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(54) Title: IMPROVED OVERBASED CARBOXYLATES

(57) Abstract

High basicity calcium carboxylates useful as lubricant and fuel additives and in paints are obtained by carbonating a mixture of a C_7 to C_{15} carboxylic preferably a branched chain oxo-acid and excess calcium at from 15 to 60 °C in the presence of a volatile solvent. Products with a basicity of from 4 to 8 may be obtained.

IMPROVED OVERBASED CARBOXYLATES

The present invention relates to new calcium soaps possessing a high basicity, more commonly called overbased calcium soaps. Overbased additives have been extensively used in engine, gear and industrial lubricants as detergent inhibitors, extreme pressure and antiwear agents, anti-corrosion and antirust additives. They can also be used as additives in fuels, as stabilizers in plastics, especially PVC, and in all sorts of anticorrosion coatings, including paints. The invention also relates to a method for preparing these overbased calcium soaps and to lubricants and fuels containing them.

The most widely known overbased calcium soaps are salts of alkylarylsulphonic acids. These are compounds which are difficult to prepare.

A traditional process for their preparation consists in reacting an alkylarylsulphonic acid with a metal oxide or hydroxide in a mineral oil. The reaction takes place in the presence of carbon dioxide (CO_2) and promoters which make the CO_2 easier to fix. The promoters are usually labile hydrogen compounds such as phenols, alcohols and aminoalcohols. When the reaction has ended, a cloudy solution (containing sediments) is obtained which is purified by centrifuging or filtration. Processes of this kind lead to calcium salts of alkylarylsulphonic acids which have a TBN (or Total Base Number) greater than or equal to 200, and capable of going up to 400 or higher. TBN is defined in ASTM standard D 2896-73.

In European Patent Application 0234149 basic calcium carboxylate soaps are described which do not possess the disadvantages of the known soaps and which have a basicity of up to 4 and yield perfectly stable and clear solutions in

oil. Basicity is the total amount of calcium in the product divided by the amount of calcium linked to the carboxylic acid.

These products are made by carbonation of an excess of calcium hydroxide dispersed in a reaction medium containing an oil-soluble organic acid, a hydrocarbon solvent, a low molecular weight alcohol, and mineral oil, followed by filtration of the unreacted materials. Carbonation is carried out in the presence of catalysts such as metal oxides and zinc carboxylates and promoters such as higher alcohols, glycols, alkyl-phenols, or amines.

These products remain in the finished product and the presence of the catalyst and oil in the finished product can limit its use.

The object of the present invention is to prepare highly overbased products which can be used in many applications, through an improved process which can lead to products free of mineral oil, and catalysts.

The present invention therefore provides a process for the production of basic calcium carboxylic acid salts comprising

i) Neutralising a C_7 to C_{15} carboxylic acid in the presence of a volatile solvent

ii) Adding excess calcium

iii) Carbonating the mixture at a temperature of from 15°C to 60°C

iv) Removal of the volatile solvent and water and adding a diluent.

The reaction is generally carried out in the absence of carbonation catalysts.

The present invention further provides an overbased calcium carboxylic acid salt having a basicity from 4 to 8.

We prefer to use the carboxylic acids described in European Patent 0234149 preferably saturated C_8, C_9 and C_{10} organic carboxylic acids which consist of isomeric mixtures and which are generally known as oxo acids. These oxo acids are characterized by a low linear acid content, generally less than or equal to 10% by weight, a low content of acids which are branched on carbon 2, generally less than or equal to 10% by weight, and a high content of acids which are mono- or polysubstituted on carbon 3 and/or carbons of higher rank, which is generally greater than 80% by weight. The oxo acids may be obtained by hydroformylation of C_7, C_8 and C_9 olefins, followed by an oxidation.

Among the organic carboxylic acids which are also suitable for the present invention there may also be added the derivatives which are mono- or polysubstituted in the 3-position and/or of higher rank of the acids corresponding to heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid and dodecanoic acid. These include, for example, 3-methylhexanoic acid, isooctanoic acid, 4,5-dimethylhexanoic acid, isononanoic acid, 3,5,5-trimethylhexanoic acid, isodecanoic acid, 3-ethyloctanoic acid, isoundecanoic acid, 4-ethylnonanoic acid and isododecanoic acid. The mixture of one or more of the above-mentioned acids, whether mixed or not with their isomers is also suitable for the present invention, it being preferred that the content of linear acids does not exceed 40% and that the content of acids which are substituted on carbon 2 does not exceed 20%. We have found that the linear acids and the acids branched on carbon 2 lead to the formation of a viscous

product, or to the reaction mixture setting solid or, alternatively, to a precipitate which considerably limits the use of the product.

In a preferred embodiment of the process of the present invention calcium oxide and/or hydroxide is reacted with carbon dioxide and at least one organic carboxylic acid by passing the carbon dioxide through the reaction mixture.The process is characterized in that the reaction is performed in at least one organic solvent at a temperature of between 15 and 60 °C, preferably 25 to 35 °C most preferably 27 to 30 °C, and the acid is a saturated organic carboxylic acid containing from 7 to 15 carbon atoms, in which the content of linear acids is preferably less than or equal to 40% by weight, in which the content of acids branched on carbon 3 and/or the carbons of higher rank is equal to or higher than 40% by weight.

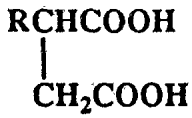
When the reaction has ended a diluent is generally added and the organic solvent and any water formed in the reaction may be removed by distillation. The product is usually filtered before or after removal of the organic solvent. The diluent may be oil or aromatic or aliphatic although an aliphatic diluent is preferred. Where the diluent is volatile it may subsequently be removed to yield a dry powdered product.

The volatile solvent preferably contains at least one nonpolar organic solvent chosen from naphtha, hexane, kerosene, benzene, toluene or xylene. It is also possible to use a mixture of paraffinic hydrocarbons of mineral or synthetic origin, preferably containing a low proportion of aromatic and/or naphthenic hydrocarbons, such as white spirit. It is preferred to also use polar organic cosolvents such as C_1 to C_6 alcohols, for example methanol, 1-butanol, 2-butanol, ethylene glycol, propylene glycol, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, diethylene

glycol and its ethers, mixtures of alcohols derived from paraffin, methyl ethyl ketone, aromatic alcohols such as phenol; amines, for example aniline, phenylenediamine, or dodecylamine; or, yet again, a mixture of alcohols and/or amines, for example of methanol and aqueous ammonia. The preferred material is methanol, which gives the highest basicities and the shortest filtration times.

The molar ratio of calcium to the organic carboxylic acid employed in the reaction is generally between 2 and 4, which corresponds to a basicity of between 4 and 8. The period of carbonation is preferably between 1 and 6 hours, preferably 4 hours, such that the hourly mass ratio of carbon dioxide to calcium hydroxide is between 0.05 and 0.5, and more preferably between 0.1 and 0.2.

Where it is desired to use the products as oil additives their oil solubility may be improved by the addition of up to 50 wt%, preferably no more than 30 wt% based on the weight of carboxylic acid, of higher molecular weight organic acids to the reaction mixture. Examples of acids include monocarboxylic acids such as oleic or stearic acid and sulphonic acids such as alkyl aryl sulphonic acids. Preferred are the dicarboxylic acids such as the substituted succinic acids having the formula



wherein R may be an olefin polymer-derived group formed by polymerization of such monomers as ethylene, propylene, 1-butene, isobutene, 1-pentene, 2-pentene, 1-hexene and 3-hexene. R may also be derived from a high molecular weight substantially saturated petroleum fraction.

The above-described classes of carboxylic acids derived from olefin polymers, and their derivatives, are well known in the art, and methods for their preparation as well as representative examples of the types useful in the present invention are described in detail in a number of U.S patents.

When dissolved in an oil, the calcium overbased soaps according to the invention can yield stable and completely clear solutions. In addition, they have a high TBN above 400, typically between 400 and 550. They find numerous applications, particularly as lubricant additives and in metal working fluids where they can impart detergent, extreme pressure, antiwear, anticorrosion and antirust properties. The metal working fluids may be straight oils, oil/water systems or totally aqueous. The calcium overbased salts may also be used as paint driers. Where the diluent is aliphatic it can be removed to produce diluent free powdered material useful as a paint additive.

The invention is illustrated by the following nonlimiting examples.

Example 1

An overbased calcium C_{8910} Cekanoic acid was prepared by the following steps.

A. Neutralisation of CEKANOIC 8910 acid with calcium hydroxide to produce neutral calcium carboxylate

- under vigorous stirring
- under cooling

CHARGES

	Parts by Weight		
1. Methanol	240.00	)	raw material addition
2. Toluene	480.00	)	and
3. Hydrated lime	257.00	)	neutralisation/cooling
4. Iso C8910 Acid	208.00	)	(max temp 28°C)

As the neutralisation is exothermic, the C8910 acid is added at a low rate in order to keep the temperature below 28°C.

B. Carbonation to about 85% of stoechiometry and heat treatment to produce colloidally dispersed calcium carbonate and hydroxide.

Carbon dioxide 100.00 parts by weight
- vigorous stirring
- CO_2 sparging
- 28°C for 4 hours.

The product which had a sediment content of about 3.0 volume% at the end of carbonation was heat soaked at from 28° to 60°C for 1 hour and then at 60°C for 15 minutes which reduced the sediment to 1 volume%.

C. Methanol/Water/Toluene Azeotrope Stripping

- in about 1.5 to 2 hours
- under NITROGEN sparging
- addition of anti-foam (droplets) as needed
- in order to decrease viscosity of the liquid phase 225.00 ml of Exxsol D100 diluent was added slowly after the stripping of the main quantity of methanol-water/ toluene azeotrope.

D. Filtration

The product was filtered at ambient temperature at 5 bars pressure during the stripping after removal of 400 grams of the azeotrope when reaching 80 to 85°C.

35 grams of the filter aid were added.

By-product

	Filter aid	35 g
	Sediments	25 g
	Diluted product	23 g
Filtrate 1012.00 g		83 g filter cake

E. Stripping to Recover the Remaining Process Solvents

- in about 1.5 to 2 hours
- under NITROGEN sparging
- under VACUUM (400 mm HG)
- maximum temperature 105°C

Product

690.00 g of finished product were obtained having the following properties:

Basicity	4.94
Calcium mass%	15.7
Kin.visco cst at 100°C	1033

Examples 2 to 17

The process of Example 1 was repeated using different acids and diluents. In Examples 13 and 14 the amount of hydrated lime used was increased to give a higher basicity. Examples

15 to 17 show the effect of using acids with different backbone structures. The properties of the products obtained are set out in the following table in which A.I means active ingredient and:

Varsol 110 is a desulphurised aliphatic hydrocarbon diluent boiling in the range 245 to 275°C, containing about 25% aromatics

STANCO 150 is a solvent neutral naphthenic paraffinic oil

PAO6 is a polyalpha olefin with kinematic viscosity of 6 centistrokes at 100°C

EXXSOL D100 is a desulphurised, dearomatised hydrocarbon diluent

SA is C_{24} alkyl benzene sulphonic acid

PIBSA is an alkenyl succinic anhydride in which the alkenyl group contains an average of 68 carbon atoms

EXAMPLE	Acid + Diluent Used Mass%	TBN	Basicity aspect	SOLUBILITY at 10% mass in STANCO 150/poly alpha olefin
Iso Cekanoates C8,9,10 in Varsol 110				
2	iso C8,9,10 100 Varsol 110 110	480	3.5 clear liquid	STANCO 150: no
3	iso C8,9,10 100 Varsol 110 110	477	4.94 hazy liquid	STANCO 150: no

Iso Cekanoates C8,9,10 in Exxsol D100				
4	iso C8,9,10 52 Pibsa 48 in Exxsol D100 100	355	4,94 hazy liquid	STANCO 150: yes PA06 : yes
5	iso C8,9,10 70 Pibsa 30 in Exxsol D100 100	447	4.94 clear liquid	STANCO 150: no
6	iso C8,9,10 55 SA 45 in Exxsol D100 100	428	4.94 liquid	STANCO 150: yes
7	iso C8,9,10 77.5 SA 22.5 in Exxsol D100 100	500	4.94 liquid	STANCO 150: no
8	iso C8,9,10 41.5 Oleic acid 58.5 in Exxsol D100 100	308	4.94 liquid/ gelling over time	STANCO 150: yes
Iso Cekanoates C13 in Exxsol D100				
9	iso C13 100 in Exxsol D100 100	512	4.94 hazy	STANCO 150: no
10	iso C13 80 Pibsa 20 in Exxsol D100 100	481	4.94 hazy	STANCO 150: yes PA06: yes
11	iso C13 80 Oleic acid 20 in Exxsol D100 100	512	4.94 hazy	STANCO 150: yes PA06: yes
12	iso C13 80 SA 20 in Exxsol D100 100	452	4.94	STANCO 150: yes PA06: yes
Iso Cekanoates Ca mass% ratio increased				
13	iso C8,9,10 100 in Exxsol D100 100	334	6.05	STANCO 150: no tacky-translucent

14	iso C13 PIBSA in Exxsol D100	80 20 100	506	6.90	STANCO 150: yes/ hazy
Acid backbone structure					
15	iso C9 in Exxsol D100	100 100	407	4.94	
16	linear C9 in Exxsol D100	100 100	paste	4.94	brittle paste translucent non tacky
17	neo C9,10 in Exxsol D100	100 100	paste	4.94	soft paste white

When the diluent was removed from the product of Examples 8 to 12 and 14 a dry film was obtained which could readily be powdered.

Various of the Products were dissolved in a base lubricating oil (STANCO 150) and the oils subjected to the Four Ball Wear Test (ASTM D 4172) and the Four Ball Extreme Pressure Test (ASTM D 2783) and compared with the commercial product LZ 5347 available from Lubrizol. The results are in the table 2.

TABLE 2 - ASTM D 2783 RESULTS

PRODUCT OF EXAMPLE	LOAD WEAR INDEX	4 BALL SEIZURE LOAD	EP WELD LOAD	%wt IN OIL
11	35.1	100 KG	160 KG	3.9%
14	43.6	126 KG	160 KG	3.9%
4	45.6	100 KG	126 KG	5.6%
12	43.1	126 KG	160 KG	4.4%
10	45	126 KG	200 KG	4.2%
LZ 5347	37.6	100 KG	200 KG	5%
LZ 5347	47.8	126 KG	250 KG	10%
STANCO 150	26.5	80 KG	126 KG	0%

ASTM D 4172 Results

The test was carried out for 60 minutes at a load of 50 kg at 75°C at 1800 rotations per minute.

PRODUCT OF EXAMPLE	WT% IN OIL	MINIMUM SCFP DIAMETER (mm)
11	3.9	1.905
4	5.6	1.87
12	4.4	0.39
10	4.2	0.355
LZ 5347	5	0.34
LZ 5347	10	0.39
	0	2.465

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the production of basic calcium carboxylic acid salts free from mineral oil and catalysts.

i) Neutralising a C_7 to C_{15} aliphatic carboxylic acid in the presence of a volatile solvent.

ii) Adding excess calcium.

iii) Carbonating the mixture at a temperature of from 15°C to 60°C.

iv) Removal of the volatile solvent and water and adding a diluent wherein the carboxylic acid comprises saturated C_8, C_9 and C_{10} oxo acids in which the oxo acids contain less than or equal to 10% by weight of acids which are branched on carbon 2, and greater than 80% by weight of acids which are mono- or polysubstituted on carbon 3 and/or carbons of higher rank, or C_7 to C_{15} acids comprising acids mono- or polysubstituted in the 3- position and/or carbons of higher rank with less from 40% by weight of linear acids and less than 20% by weight of acids substituted on carbon 2.

2. A process according to claim 1 in which up to 50 wt% of an organic acid of higher molecular weight than the C_9 to C_{15} acid is added to the reaction mixture.

3. A process according to any one of the preceding claims in which the volatile solvent contains at least one nonpolar organic solvent chosen from naphtha, hexane, kerosene, benzene, toluene or xylene.

4. A process according to claim 3 in which the volatile solvent also contains organic cosolvents chosen from C_1 to C_6 alcohols, for example methanol, 1-butanol, 2-butanol, ethylene glycol, propylene glycol, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether or dethylene glycol.

5. A process according to any one of the preceding claims to which the molar ratio of calcium to the organic carboxylic acid is between 2 and 4.

6. A process according to any one of the preceding claims including the additional step of removing the diluent.

7. A process according to any one of the preceding claims in which the temperature of carbonation is in the range 25°C to 35°C.

8. An overbased calcium carboxylic acid salt, free from mineral oil and catalysts, having a basicity from 4 to 8, in which the carboxylic acid comprises a saturated C_8, C_9 and C_{10} oxo acid in which the oxo acid contains less than or equal to 10% by weight of linear acid, less than or equal to 10% by weight of acids which are branched on carbon 2, and greater than 80% by weight of acids which are mono- or polysubstituted in the 3- position and/or carbons of higher rank, with less than 40% by weight of linear acids and less than 20% by weight of acids substituted on carbon 2.

DATED this 30th day of March, 1995.
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DBM/LPS/ML DOC:2 AU2692592.WPC

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 92/02328

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C10M159/20; //(C10N40:20)

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C10M

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US,A,2 865 956 (GLYN ELLIS) 23 December 1958 see column 5, line 68 - column 6, line 21 see column 7, line 75 - column 8, line 2	1,5-9,11
X	EP,A,0 248 465 (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ) 9 December 1987	1,5,6
A	see page 2, line 44 see page 4; example 1	9,11
X	DE,B,1 123 324 (BATAAFSE PETROLEUM MAATSCHAPPIJ) 8 February 1962 see column 8, line 36 - line 41; example 3	9,10,11

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* Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

"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

IV. CERTIFICATION

1

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
16 DECEMBER 1992	18. 01. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	HILGENGA K.J.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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A	US,A,4 100 084 (W.J POWERS) 11 July 1978	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9202328 SA 65399

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 16/12/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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