

Description

The present invention relates to a process for the preparation of a basic alkaline earth metal salt of a blend of organic carboxylic acids, a salt thus prepared and to oil compositions containing such a salt.

The use of alkaline earth metal salts of organic carboxylic acids as additives for lubricating oil compositions is known. The said salts have a dispersant property so that, when applied in such composition, they ensure that the inside of engine cylinders remains clean and that deposition of carbonaceous products on pistons and in piston grooves is counteracted, so that piston-ring sticking is prevented.

It is also known to prepare basic (or overbased) alkaline earth metal salts of such acids. The overbasing provides an alkaline reserve which, when applied in lubricating oil compositions, reacts with and neutralizes acidic compounds formed during the operation of the engine in which the composition is applied. Hence, sludge which may arise is maintained dispersed due to the dispersant property of the salt while acids which would enhance sludge formation are neutralized.

British patent specification No. 786,167 describes a process for the preparation of basic salts in which an organic acid is reacted with an excess of an alkaline earth metal oxide or hydroxide in an oil and subsequently carbon dioxide is passed through the reaction mixture to yield basic salts. As suitable acids are mentioned substituted or unsubstituted aliphatic, cycloaliphatic and aromatic acids, comprising carboxylic acids, sulphur-containing acids, phosphoric acids, thio-acids, phenols and partial esters of sulphur- and phosphorus-containing acids.

The incorporation of basic salts into lubricating oil compositions in some cases gives rise to problems. One of these problems is that the lubricating oil compositions tend to form haze on standing. Haze may occur by a phase separation between the basic salt complexes and the base oil, which may lead to precipitation of the complexes. This problem is more pronounced now that many lubricating base oils have been subjected to hydro-cracking and/or hydrotreating.

A solution for this problem proposed in GB-A-1,290,251 is to add to the basic-salt containing lubricating oil composition an aliphatic carboxylic acid or anhydride having at least 23 aliphatic carbon atoms per carboxy group. Examples of such an acid or anhydride include hydrocarbon-substituted succinic acids or anhydrides having at least 50 aliphatic carbon atoms. The latter acids and anhydrides are described in e.g. UA-S-3,219,666. However the addition of such acids or anhydrides to the pre-formed lubricating oil composition does not always eliminate the haze entirely.

Applicants have now surprisingly found that when an aliphatic acid or anhydride is present during the preparation of the basic salt, a stable, clear solution is obtained in which no haze occurs. Accordingly, the present invention provides a process for the preparation of basic alkaline earth metal salts of organic carboxylic acids, which comprises :

- (a) blending an oil-soluble alkyl salicylic acid with one or more long-chain hydrocarbon-substituted derivatives of succinic acid or succinic anhydride in which the hydrocarbon substituent has a number average molecular weight from 120 to 5000,
- (b) mixing the blend of acids with more than an equivalent amount of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent ;
- (c) introducing carbon dioxide into the mixture obtained in an amount of at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal ; and
- (d) removing residual solids, if any, and an aqueous layer, if any.

The alkyl salicylic acid used in the process of the present invention is oil-soluble due to presence of the alkyl substituent or substituents. The number of such substituents may be more than one, e.g. two or three, and the number of carbon atoms in each alkyl substituent is suitably at least four, and preferably ranges from 8 to 30. When the alkyl salicylic acid contains predominantly only one alkyl substituent, that preferably contains from 12 to 26 carbon atoms. The alkyl group(s) may be linear or branched, but are suitably linear.

The long-chain hydrocarbon substituent in the succinic acid or anhydride derivative is preferably an oligomer or polymer derived from an olefin, and containing at least 10 carbon atoms. When the substituent is an oligomer, this may be based on from 3-12 monomer units, with higher chain lengths being regarded as polymers. The polymers may be homopolymers or copolymers of one or more olefin monomers, such copolymers including random, block and tapered copolymers. Preferred olefin monomers are those having 2 to 16 carbon atoms, preferably from 2 to 6 carbon atoms, such as ethene, propene, butenes, isobutenes, pentenes, octenes, and also diolefines such as butadiene and isoprene. If a diene is used as monomer the resulting oligomer or polymer is preferably hydrogenated to saturate at least 90%, more preferably substantially all unsaturated bonds. Conveniently the hydrocarbon substituent is a linear oligomer or polymer derived from ethylene, or a

branched one derived from propene or isobutylene.

Particularly suitable oligomeric long-chain hydrocarbon substituents are the higher olefins derived from oligomerisation of ethylene (eg. as in the Shell Higher Olefins Process "SHOP"), especially those containing 14 to 18 carbon atoms, and also oligomers of propylene, such as propylene tetramer. Particularly suitable polymeric long chain hydrocarbon substituents are those derived from isobutylene.

As previously mentioned the average number molecular weight of the long-chain hydrocarbon substituent should be from 120 to 5000, and is preferably from 150 to 1500. The number average molecular weight (M_n) can easily be determined by vapour pressure osmometry or by gel permeation chromatography with calibration of the polymer, as will be appreciated by those skilled in the art. The weight average molecular weight (M_w) can also be determined by gel permeation chromatography. The quotient M_w/M_n , which is a measure indicating the width of molecular weight distribution, has usually a value from 1.5 to 4.0.

The average number of succinic groups per hydrocarbon group may be greater than 1. This means that then at least some hydro-carbon moieties are connected to at least two succinic groups. Preferably, the average number of succinic groups per hydrocarbon group is between 0.5 and 3.

The preparation of hydrocarbon-substituted succinic anhydride is known in the art. In case a polyolefin is used as substituent substituted succinic anhydride can conveniently be prepared by mixing the polyolefin, e.g. polyisobutylene, with maleic anhydride and passing chlorine through the mixture yielding hydrochloric acid and alkenyl-substituted succinic anhydride, as described in e.g. GB-A-949,981.

Another method of the preparation of substituted succinic anhydride is described in US-A-3,172,892, according to which a halogenated, in particular chlorinated, polyolefin is reacted with maleic anhydride.

From e.g. NL-A-7412057 it is known to prepare hydrocarbon-substituted succinic anhydride by reacting thermally a polyolefin with maleic anhydride. It is further possible to combine the methods of this Dutch application and GB-A-949,981, as is illustrated in GB-A-1,440,219 and GB-A-1,543,627. The products prepared in this way include compounds in which the alkenyl chain is connected to one or both of the alpha carbon atoms of the succinic group.

Similar processes can be used to prepare succinic derivatives bearing an oligomer substituent. The ratios between the alkyl salicylic acid and the hydrocarbon-substituted succinic acid or anhydride may vary within wide ranges. Advantageously the equivalent ratio of the alkyl salicylic acid to hydrocarbon-substituted succinic acid or anhydride ranges from 15 : 1 to 1 : 10, preferably from 4 : 1 to 1 : 1.

The alkaline earth metal salts prepared include magnesium, calcium, strontium and barium salts. Preferably, the alkaline earth metal is magnesium or calcium.

The reaction mixture prepared in step (b) of the present process suitably contains a promotor, preferably an oxygen-containing organic solvent and optionally water. Suitable solvents include C_{1-6} alcohols, polyhydric alcohols such as glycol, propylene glycol, glycerol or 1,3-dihydroxypropane, ethers such as C_{1-4} monoethers of glycol or propylene glycol, diisopropyl ether, 1,3- or 1,4-dioxane, or 1,3-dioxolane. Preferably the promotor is a C_{1-6} alcohol, in particular methanol. It will be appreciated that in industrial processes use may be made of technical solvents, and that the use of technically pure promotors, such as methanol, might introduce the presence of water. Hence, in such cases addition of water per se is not required since its addition is made implicitly by the addition of the promotor.

The preparation of the mixture according to step b) of the present process can be carried out in any convenient way, e.g. by mixing the alkaline earth metal hydroxide and/or oxide with the promotor, if used, and adding the blend of acids, whether or not in the presence of the promotor or a hydrocarbon solvent, to the resulting mixture. It is preferred to mix the blend of the acids and the alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent and subsequently add the promotor. The promotor may contain a substantial amount of water, whose content is preferably adjusted such that the percentage of water in the mixture amounts to 0 to 10%w, based on the total liquids.

The hydrocarbon solvent can be selected from a wide variety of solvents. Suitable solvents include hydrocarbon oils, such as solvent-refined and/or hydrogenated lubricating oils having a kinematic viscosity of 3.5-35mm²/s at 100°C. Preferably it is an aromatic hydrocarbon or a hydrocarbon fraction rich in aromatics, such as gasoline. Suitable hydrocarbon solvents are benzene, toluene, xylene or mixtures thereof, xylene being particularly preferred. The amount of the solvent is not critical. Promotor : solvent volume ratios up to 1 can suitably be applied, preference being given to ratios in the range from 0.1 to 0.6.

The concentration of the organic carboxylic acids in the solvent or solvent mixture can vary within wide limits. Suitably the acids equivalent concentration is from 0.01. to 1 molar equivalent/kilogram, preferably from 0.1 to 0.8, based on the combined weight of organic carboxylic acids and hydrocarbon solvent.

The amount of alkaline earth metal to be added in stage b) should be at least 1 equivalent, and is preferably more so that the subsequent carbon dioxide supply results in very basic compounds. The basicity of the products is generally the basicity index (BI), being defined as the equivalents ratio of the total of alkaline earth

metal to the total of organic acids. For a high BI the amount of alkaline earth metal hydroxide and/or oxide added in stage b) is preferably from 10 to 25 equivalents per equivalent acid.

The temperature at which stage b) is carried out is not critical, and may be ambient temperature or elevated temperature. Suitable temperatures include 15-150°C.

5 In stage c) the temperature is advantageously from 15 to 150°C, preferably from 30 to 110°C. In order to obtain the elevated temperature it may be necessary to employ elevated pressures, since the desired reaction temperature may be above the atmospheric reflux temperature of the reaction mixture. Suitable pressures include between 1 and 15 bar abs. Higher pressures are possible, but merely add to the costs of the process. The rate at which the carbon dioxide is introduced is advantageously from 0.05 to 1.0 equivalent carbon dioxide
10 per equivalent acid per minute. The carbon dioxide introduction is conveniently carried out by passing carbon dioxide, or a mixture of carbon dioxide with an inert gas, such as air or nitrogen, through the reaction mixture under slightly higher pressure than the pressure prevailing in the reaction mixture. Higher pressures may be employed. Carbon dioxide will be absorbed in the reaction mixture and will react with the alkaline earth metal compounds present therein forming a basic complex salt of the organic acid salt and carbonate, hydroxide
15 and/or oxide. The amount of carbon dioxide to be taken up in stage c) is to a certain extent dependent on the amount of alkaline earth metal added in stage b) of the present process. Suitably the relative amount of carbon dioxide is somewhat less than the relative amount of alkaline earth metal hydroxide or oxide.

Preferably the introduction of carbon dioxide in stage c) is stopped after 0.5 to 0.9 equivalent carbon dioxide per equivalent alkaline earth metal has been taken up. Conveniently, this corresponds with 5 to 23 equivalent
20 carbon dioxide per equivalent acid for high BI's mentioned above.

It has been found that an ageing period between stage c) and stage d) can be advantageous, since it increases the BI of the resulting basic salt. Such an ageing period amounts suitably to at least 15 min. A maximum period is generally imposed by practical and/or economical reasons, and is generally below 20 hours. Preferably the period between stages c) and d) is from 1 to 4 hrs.

25 The reaction mixture at the end of stage c) may be worked up by any method known in the art. It may be subjected to a centrifuging treatment to remove solids comprising unreacted alkaline earth metal hydroxide and/or oxide and/or non-colloidal alkaline earth metal carbonate, if any. The resulting solution may then be subjected to a liquid-phase separation. One liquid phase can be an aqueous layer which may contain the promotor when it is used, the other one is the hydrocarbon solvent plus the basic salts dispersed therein. It is also possible
30 to reverse the above operations.

The present process can be used for the preparation of basic salts having a wide variety of basicity indices. It can, therefore, be used to prepare basic salts having a relatively low BI e.g. from 1 to 10, but is also suitable for preparing basic salts having a basicity index from 10 to 20.

35 The process described is a one-step process. However it is possible to operate the process according to the present invention in a two-step process, in particular in a two step process according to Applicants' UK application No. 8613815. This is particularly advantageous when basic salts with a high BI are to be prepared. Thereto, stages (b) and (c) are carried out in two stages, b1, b2, c1, and c2 respectively, wherein the stages comprise :

- 40 (b1) preparing a mixture of the blend of the organic carboxylic acids with more than an equivalent amount of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent ;
- (c1) introducing carbon dioxide into the mixture obtained until at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal has been taken up ;
- 45 (b2) adding at least one further equivalent of alkaline earth metal hydroxide and/or oxide to the reaction mixture, so that the total amount of alkaline earth metal hydroxide and/or oxide is at least 10 equivalent ;
- (c2) resuming the introduction of carbon dioxide to the resulting mixture.

50 Between stages (c1) and (b2) and after (c2) ageing periods can be employed as is indicated in the above patent application. The ageing period after stage (c2) corresponds with the above-mentioned ageing period between stages (c) and (d).

The process according to the present invention can be carried out batchwise and also in a continuous manner.

55 The basic salts are excellent detergent additives in oils. Therefore the present invention also provides oil compositions comprising a major amount of a base oil and a minor amount of a basic alkaline earth metal salt as described hereinbefore. Preferably the base oil is a lubricating base oil, and conveniently constitutes more than 50%w of the composition. It can be selected from mineral lubricating oils of varying viscosities, but it also includes a synthetic lubricant, such as ester-type lubricant or a polyolefin-type fluid, or a vegetable oil, or a

grease.

Fuel compositions which are used in marine diesel engines usually contain some sulphur compounds. To neutralize the acidic compounds formed from these sulphur compounds a relatively high concentration of the basic salt is employed. Preferably, these marine lubricating oil compositions contain from 5 to 30%w of basic alkaline earth metal salt. Lubricating oil compositions for road engines may contain lower concentrations. The amount of basic alkaline earth metal salt in these lubricating oil compositions is preferably from 0.01 to 5%w, in particular from 0.1 to 4.0%w.

Fuels, such as gasoline, kerosine, diesel fuel and gas oils, can also contain the above basic salts. The amount of these salts is similar to that in road engine lubricating oil compositions or lower; conveniently the amount is from 0.001 to 5%w, in particular from 0.01 to 1.0%w.

The lubricating oil composition can be prepared by mixing a concentrate containing up to 60%w of a basic salt as described above in a lubricating oil, with a lubricating base oil to give the desired concentration. Such a concentrate is conveniently prepared by addition of a lubricating oil to the product obtained after completion of stage d), and removal of any volatile hydrocarbon solvent, water and alcohol, if present. The lubricating oil may be the same as the one indicated above as a suitable hydrocarbon solvent. The concentrate may conveniently contain a stabiliser, which is selected from a variety of organic compounds, such as those described in British patent specification No. 818,325. These compounds include mono- or polyhydric alcohols, alkyl amines and alkyl phenols.

The lubricating oil compositions may further contain a number of other additives, such as antioxidants, foam inhibitors, corrosion inhibitors, viscosity index improvers, and pour point depressants as can be established by a person skilled in the art.

The invention will be illustrated by means of the following Examples.

EXAMPLE I

225 g of a 60%w solution of C_{14-18} alkyl salicylic acid (ASA) in xylene (0.297 eq) was blended with 51 g polyisobutenyl-substituted succinic acid (PSA) (0.099 eq) in xylene (714 g), in which the polyisobutenyl radical had a number average molecular weight of 1000. 278 g calcium hydroxide was added to this mixture resulting in an equivalent ratio of 19 eq $Ca(OH)_2$ /eq acid. 166 g methanol (containing 3%w of water) was added to this mixture, which was then heated to the reaction temperature, 85°C, and stirred for 1 h, during which neutralization took place. Subsequently carbon dioxide was introduced at a rate of 0.12 eq CO_2 /eq acid/min, until the uptake of CO_2 reached 13 eq CO_2 /eq acid. The reaction mixture was then subjected to an ageing period of 16 h at a temperature of 58°C under stirring, after which the reaction mixture was allowed to settle, yielding two liquid phases, and the methanol-water layer formed was separated. Residual solids were removed from the xylene layer by centrifugation. The basicity index of the salt in the xylene layer, determined by acidimetric titration, was 14.5.

195.6 g of the product obtained was introduced into 300 g of a hydrotreated mineral lubricating oil, and the mixture obtained was subjected to vacuum distillation to remove xylene, yielding a composition containing 10.0%w calcium.

EXAMPLE II

This example illustrates the process according to the present invention carried out in a continuous manner. ASA, PSA and $Ca(OH)_2$ in an equivalent ratio of 0.75 : 0.25 : 19, in a methanol/xylene solution were continuously fed via a neutralization vessel into a carbonation vessel. The concentration of the acids and the calcium hydroxide in the liquid phase was 0.4 eq/kg, and 7.6 eq/kg respectively. The xylene/methanol (which contained 3%w of water) ratio was 4.33. The average residence time of the mixture in the neutralization and carbonation vessels was 100 minutes. CO_2 was introduced into the carbonation vessel at a rate of 0.12 eq CO_2 /eq acid per minute and at a temperature of 100°C, and reaction product was withdrawn from the carbonation vessel such that the overall composition remained the same.

Samples were drawn from the reaction product periodically, and taken up in an oil composition as described in Example 1. Sample 1 was drawn after 4 hours, and Sample 2 after 7 hours. They were taken up into a lubricating oil by the method described in Example 1. Sample 3, drawn at the same time as Sample 2 was subjected to an ageing period of 18 h at 55°C under stirring before being taken up in an oil composition. The BI's of the salts were 12.0 (Sample 1), 16.4 (Sample 2) and 17.6 (Sample 3) and the calcium contents 11.5, 13.7 and 15.0%w, respectively.

EXAMPLE IIA

The following continuous process was similar to Example II, but employed a higher ASA/PSA ratio. ASA, PSA and Ca(OH)₂ in an equivalent ratio 0.923 : 0.077 : 20, in a methanol/xylene solution were continuously fed via a neutralization vessel into a carbonation vessel. The concentration of the acids and the Ca(OH)₂ in the liquid phase was 0.4 eq/kg and 8.0 eq/kg respectively. The xylene/methanol (which contained 3%w of water) ratio was 4.33. Average residence times of the mixture in the neutralization and carbonation vessels were resp 60 and 30 minutes. Into the carbonation vessel CO₂ was introduced at a rate of 0.42 eq CO₂/eq minute and at a temperature of 55°C. A sample was drawn from the reaction mixture after 2 hours (Sample 1) and taken up in an oil composition as described in Example I. The basicity index of the salt was 13.3.

EXAMPLE III**Formation of haze and/or deposits in the compositions**

In order to assess the formation of haze and/or deposits, the products were diluted with mixture of hydrotreated lubricating oils to give a total base number of 70 mg KOH/g. These solutions were stored in tubes at ambient temperature or at 100°C and after 2 and 7 days they were visually assessed for amount of deposits and for brightness. The amount of deposits was expressed in % by volume. The brightness was classified as "bright" (B), "slightly hazy" (sH), "hazy" (H) and "muddy" (M). By "muddy" is understood the situation that the whole test tube is cloudy and that no visual assessment of the amount of deposits is possible.

The results of the measurements are shown in the Table I below.

TABLE I

Product of Example	BI	Stability (% vol deposits/brightness)	
		ambient temperature	
		2 days	7 days
I	14.7	O/B	O/B
II, sample 1	12.0	O/B	O/B
II, sample 2	16.4	O/B	O/B
II, sample 3	17.6	O/sH	O/sH
IIA	13.3	O/B	O/B

Comparative Experiment

An experiment similar to Example II was carried out, but using only ASA. Samples were drawn after 4 and 7 h and at 7h with an ageing period. The samples were taken up in lubricating oil, and subjected to the same tests as described in Example III.

Results of the tests and some data on the samples are shown in Table II.

TABLE II

Sample	After time h	Stability (%vol deposits/ brightness ambient temperature)		
		BI	2days	7days
1a	4	13.7	M	M
2a	7	15.5	M	M
3a	7+	16.1	M	M

ageing period

Samples 1a, 2a and 3a were diluted with lubricating oil to a Ca content of 10%w, and 6%w polyisobutenyl-substituted succinic acid (molecular weight of polyisobutenyl substituent about 1000) was added, thereby lowering the BI. The BI and the results of the stability tests are indicated in Table III.

TABLE III

Sample	PSA %w	Ratio ASA/PSA	BI	Stability (%vol deposits/brightness) ambient temperature	
				2days	7days
1a	6	5.24	11.5	O/H	O/H
2a	6	4.63	12.8	M	M
3a	6	4.46	13.2	M	M

It is apparent that, although the addition of PSA marginally improves the stability of sample 1a, the overall results are still unsatisfactory and greatly inferior to those of Table I (representing the present invention).

EXAMPLE IV

Further products were prepared following a batch procedure similar to Example I, but using as the ASA a salicylic acid substituted by propylene tetramer or a C₁₄₋₁₈ higher olefin (from SHOP process) and, in some experiments replacing the PSA with succinic acid substituted by a C₁₈ higher olefin (from SHOP process). Different acid, calcium hydroxide and carbon dioxide intakes were used to obtain products with BI's in the range 2.6-3.4. The properties of these products were compared with corresponding materials in which the PSA was added after the overbasing process (Products 4x and 4y) and with the corresponding material to which no PSA was added (Product 4z), and the results are set out in Table IV below.

TABLE IV

Product	Acid Blend		C ₁₈ SHOP Succinic acid	PSA	Blend Stability	
	ASA alkyl group (t eq/eq)	C ₁₄₋₁₈ SHOP			added after	at 100°C
	Propylene Tetramer				overbasing	2 Days 7 Days
4a	75			25	O/B	O/B
4b	85.7			14.3	O/B	O/B
4c		75	25		O/B	O/B
4x	100			15.8*	O/B	O/B
4y	100			7.9**	O/B	tr/H
4z	100			0.0	1.6/B	1.2/B

* Corresponds to 3/1 ASA/PSA ratio of 4a

** Corresponds to 6/1 ASA/PSA ratio of 4b

Claims

- 5 1. Process for the preparation of basic alkaline earth metal salts of organic carboxylic acids, which comprises
- (a) blending an oil-soluble alkyl salicylic acid with one or more long-chain hydrocarbon-substituted derivatives of succinic acid or succinic anhydride in which the hydrocarbon substituent has a number average molecular weight from 120 to 5000,
- 10 (b) mixing the blend of acids with more than an equivalent amount of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent ;
- (c) introducing carbon dioxide into the mixture obtained in an amount of at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal ; and
- 15 (d) removing residual solids, if any, and an aqueous layer, if any.
2. Process as claimed in claim 1, in which the alkyl salicylic acid has 12 to 26 carbon atoms in the alkyl group.
3. Process as claimed in claim 1 or 2, in which the long-chain hydrocarbon substituent in the succinic acid or anhydride is an oligomer or polymer derived from an olefin, and containing at least 10 carbon atoms.
- 20 4. Process as claimed in claim 3, wherein the long-chain hydrocarbon substituent is a propylene tetramer, a C₁₄-C₁₈ olefin obtained from ethylene oligomerisation, or a polyisobutylene.
5. Process as claimed in any one of claims 1-5 in which the number average molecular weight of the long-chain hydrocarbon substituent is from 150 to 1500.
- 25 6. Process as claimed in any one of claims 1 to 5, in which the equivalent ratio of the alkyl salicylic acid to the long-chain hydrocarbon-substituted succinic acid or anhydride ranges from 15 : 1 to 1 : 10.
7. Process as claimed in claim 1-6, in which the alkaline earth metal is magnesium or calcium.
8. Process as claimed in any one of claims 1-7, in which the mixture in stage (b) further comprises an oxygen-containing organic solvent, and optionally water.
- 30 9. Process according to any one of claims 1-8, in which the mixture of the blend of acids and alkaline earth metal hydroxide and/or oxide is prepared by mixing the acids and the alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent.
10. Process according to any one of claims 1-9, in which stages (b) and (c) are carried out in two stages, the stages comprising :
- 35 (b1) preparing a mixture of the blend of organic carboxylic acids with more than an equivalent amount of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent ;
- (c1) introducing carbon dioxide into the mixture obtained until at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal has been taken up ;
- 40 (b2) adding at least one further equivalent of alkaline earth metal hydroxide and/or oxide to the reaction mixture, so that the total amount of alkaline earth metal hydroxide and/or oxide is at least 10 equivalent ;
- (c2) resuming the introduction of carbon dioxide to the resulting mixture.
- 45 11. Basic alkaline earth metal salt of a blend of organic carboxylic acids whenever prepared according to any one of claims 1-10.
12. Oil composition comprising a major amount of base oil and a minor amount of a basic alkaline earth metal salt according to claim 11.

Patentansprüche

1. Verfahren zur Herstellung von basischen Endalkalimetallsalzen von organischen Carbonsäuren, umfassend :

- 55 (a) Mischen einer öllöslichen Alkylsalicylsäure mit einem oder mit mehreren, durch lange Kohlenwasserstoffketten substituierten Derivaten von Bernsteinsäure oder Bernsteinsäureanhydrid, worin der Kohlenwasserstoffsubstituent ein zahlenmäßiges mittleres Molekulargewicht von 120 bis 5.000 aufweist,



- (b) Vermischen des Säuregemisches mit mehr als einer äquivalenten Menge eines Erdalkalimetallhydroxids und/oder -oxids in einem Kohlenwasserstofflösungsmittel ;
- (c) Einführen von Kohlendioxid in das erhaltene Gemisch in einer Menge von wenigstens 0,5 Äquivalenten Kohlendioxid je Äquivalent überschüssigem Erdalkalimetall ; und
- (d) Abtrennen verbliebener Feststoffe, sofern vorhanden, und einer wäßrigen Phase, sofern vorhanden.

2. Verfahren nach Anspruch 1, worin die Alkylsalicylsäure 12 bis 26 Kohlenstoffatome in der Alkylgruppe aufweist.

3. Verfahren nach Anspruch 1 oder 2, worin der langkettige Kohlenwasserstoffsubstituent in der Bernsteinsäure oder im Bernsteinsäureanhydrid ein von einem Olefin abgeleitetes Oligomer oder Polymer ist und wenigstens 10 Kohlenstoffatome enthält.

4. Verfahren nach Anspruch 3, worin der langkettige Kohlenwasserstoffsubstituent ein Propylentetramer, ein aus der Ethylenoligomerisation erhaltenes C₁₄-C₁₈ Olefin oder ein Polyisobutylen ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, worin das zahlenmäßige mittlere Molekulargewicht des langkettigen Kohlenwasserstoffsubstituenten 150 bis 1.500 beträgt.

6. Verfahren nach einem der Ansprüche 1 bis 5, worin das Äquivalentverhältnis der Alkylsalicylsäure zu der durch einen langkettigen Kohlenwasserstoff substituierten Bernsteinsäure oder dem Bernsteinsäureanhydrid im Bereich von 15 : 1 bis 1 : 10 liegt.

7. Verfahren nach Anspruch 1 bis 6, worin das Erdalkalimetall Magnesium oder Calcium ist.

8. Verfahren nach einem der Ansprüche 1 bis 7, worin das Gemisch in Stufe (b) zusätzlich ein sauerstoffhaltiges organisches Lösungsmittel und gegebenenfalls Wasser umfaßt.

9. Verfahren nach einem der Ansprüche 1 bis 8, worin das Gemisch aus dem Säuregemisch und dem Erdalkalimetallhydroxid und/oder -oxid durch Vermischen der Säuren und des Erdalkalimetallhydroxids und/oder -oxids in einem Kohlenwasserstofflösungsmittel bereitet wird.

10. Verfahren nach einem der Ansprüche 1 bis 9, worin die Stufen (b) und (c) in zwei Stufen ausgeführt werden, wobei diese Stufen umfassen :

(b1) Herstellen eines Gemisches aus dem Gemisch von organischen Carbonsäuren mit mehr als einer äquivalenten Menge eines Erdalkalimetallhydroxids und/oder -oxids in einem Kohlenwasserstofflösungsmittel ;

(c1) Einführen von Kohlendioxid in das erhaltene Gemisch, bis wenigstens 0,5 Äquivalente Kohlendioxid je Äquivalent überschüssigem Erdalkalimetall aufgenommen worden sind ;

(b2) Zusetzen wenigstens eines weiteren Äquivalents von Erdalkalimetallhydroxids und/oder -oxid zu dem Reaktionsgemisch, sodaß die Gesamtmenge an Erdalkalimetallhydroxid und/oder -oxid wenigstens 10 Äquivalente beträgt ;

(c2) Wiederaufnehmen der Einführung von Kohlendioxid in das gebildete Gemisch.

11. Basisches Erdalkalimetallsalz eines Gemisches aus organischen Carbonsäuren, wann immer es nach einem der Ansprüche 1 bis 10 hergestellt ist.

12. Ölzusammensetzung mit einem Hauptanteil eines Grundöles und einer kleinen Menge eines basischen Erdalkalimetallsalzes nach Anspruch 11.

Revendications

1. Procédé de préparation de sels basiques de métal alcalino-terreux d'acides organiques carboxyliques, qui comprend :

a) le mélange d'un acide alkylsalicylique soluble dans l'huile avec un ou plusieurs dérivés d'acide succinique ou d'anhydride succinique substitués par un hydrocarbure à chaîne longue, dans lesquels le substituant hydrocarbure a un poids moléculaire en nombre moyen compris entre 120 et 5000,

b) le mélange du mélange d'acides avec plus d'une quantité équivalente d'un oxyde et/ou hydroxyde de métal alcalino-terreux dans un solvant hydrocarbure ;

c) l'introduction de dioxyde de carbone dans le mélange obtenu selon une quantité d'au moins 0,5 équivalent de dioxyde de carbone par équivalent d'excès de métal alcalino-terreux ; et

d) l'élimination de solides résiduels, s'il y en a, et d'une couche aqueuse, s'il y en a.



2. Procédé selon la revendication 1, dans lequel l'acide alkylsalicylique a entre 12 et 26 atomes de carbone dans le groupe alkyle.

3. Procédé selon la revendication 1 ou 2 dans lequel le substituant hydrocarbure à longue chaîne dans l'acide ou l'anhydride succinique est un oligomère ou un polymère dérivé d'une oléfine et contenant au moins 10 atomes de carbone.

4. Procédé selon la revendication 3, dans lequel le substituant hydrocarbure à longue chaîne est un propylène tétramère, une oléfine C_{14} - C_{18} obtenu par oligomérisation de l'éthylène, ou un polyisobutylène.

5. Procédé selon l'une quelconque des revendications 1-5 dans lequel le poids moléculaire moyen en nombre du substituant hydrocarbure à longue chaîne est compris entre 150 et 1500.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la proportion équivalente de l'acide alkylsalicylique à l'acide ou anhydride succinique substitué par un hydrocarbure à longue chaîne est comprise entre 15 : 1 et 2 : 10.

7. Procédé selon l'une des revendications 1-6, dans lequel le métal alcalino-terreux est le magnésium ou le calcium.

8. Procédé selon l'une quelconque des revendications 1-7, dans lequel le mélange à l'étape (b) comprend en plus un solvant organique contenant de l'oxygène, et éventuellement de l'eau.

9. Procédé selon l'une quelconque des revendications 1-8, dans lequel on prépare le mélange d'acides et d'hydroxyde et/ou l'oxyde de métal alcalino-terreux en mélangeant les acides et l'hydroxyde et/ou l'oxyde de métal alcalino-terreux dans un solvant hydrocarbure.

10. Procédé selon l'une quelconque des revendications 1-9, dans lequel on réalise les étapes (b) et (c) en deux étapes, les étapes comprenant :

(b1) la préparation d'un mélange des acides organiques carboxyliques avec plus d'une quantité équivalente d'hydroxyde et/ou d'oxyde de métal alcalino-terreux dans un solvant hydrocarbure ;

(c1) l'introduction de dioxyde de carbone dans le mélange obtenu jusqu'à ce qu'au moins 0,5 équivalent de dioxyde de carbone soit observé par équivalent de métal alcalino-terreux ;

(b2) l'addition d'au moins un autre équivalent d'hydroxyde et/ou d'oxyde de métal alcalino-terreux au mélange réactionnel, de sorte que la quantité totale d'hydroxyde et/ou d'oxyde de métal alcalino-terreux soit d'au moins 10 équivalents ;

(c2) l'arrêt de l'introduction de dioxyde de carbone au mélange résultant.

11. Sel basique de métal alcalino-terreux d'un mélange d'acides carboxyliques organiques préparé selon l'une quelconque des revendications 1-10.

12. Composition d'huile comprenant une quantité majeure d'une huile de base et une quantité mineure d'un sel basique de métal alcalino-terreux selon la revendication 11.

