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OVERBASED CALIXARATES, PROCESS FOR THEIR PRODUCTION,
COMPOSITIONS CONTAINING THEM AND USE AS LUBRICATING OIL ADDITIVES

The present invention relates generally to overbased metal salts, their preparation and their use as detergent additives in lubricating oil compositions.

In the operation of the internal combustion engine by-products from the combustion chamber often blow by the piston and admix with the lubricating oil.

Compounds generally employed to neutralise the acidic materials and disperse sludge within the lubricating oil are the overbased alkaline earth metal sulphurised hydrocarbyl-substituted phenates, salicylates, napthenates and sulphonates. The term "overbased" is generally used to describe those alkaline earth metal hydrocarbyl-substituted salts in which the ratio of the number of equivalents of the alkaline earth metal moiety to the number of equivalents of the acid moiety is greater than one, and is usually greater than 1.2 and may be as high as 4.5 or greater. In contrast, the equivalent ratio of alkaline earth metal moiety to acid moiety in "normal" or "neutral" alkaline earth metal hydrocarbyl-substituted salts is one, and in "low based" salts is less than one. Thus, the overbased material usually contains greater than 20% in excess of the alkaline earth metal present in the corresponding neutral material. For this reason overbased alkaline earth metal hydrocarbyl-substituted salts have a greater capability for neutralising acidic matter than do the corresponding neutral alkaline earth metal hydrocarbyl-substituted salts, though not necessarily an increased detergency power.

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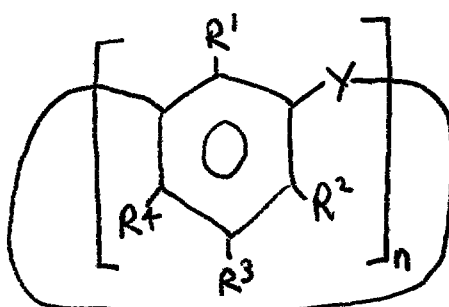


In the manufacture of the aforesaid sulphurised hydrocarbyl phenates, hydrogen sulphide is generated, which hydrogen sulphide is generally disposed of by burning, thereby producing sulphur dioxide, which is released to the atmosphere. Environmental concerns are growing over the use of sulphur-containing lubricant additives, due to the resulting sulphur dioxide emissions associated with lubricant combustion in service, as well as in additive production. In consequence, a desirable objective would be to develop sulphur-free overbased alkaline earth metal salts suitable for use as detergent additives in lubricating oils.

In furtherance of this objective the present invention in one aspect provides a non-sulphurised overbased metal salt of a sulphur-free calixarene having a substituent hydroxyl group or groups available for reaction with metal base.

For a review of calixarenes the reader is referred to 'Monographs in Supramolecular Chemistry' by C David Gutsche, Series Editor - J Fraser Stoddart, published by the Royal Society of Chemistry, 1989. Calixarenes having a substituent hydroxyl group or groups include homocalixarenes, oxacalixarenes, homooxacalixarenes and heterocalixarenes.

Suitable calixarenes may be represented by the formula:



(I)

wherein Y is a divalent bridging group;

R³ is a hydrocarbyl or a hetero-substituted hydrocarbyl group;

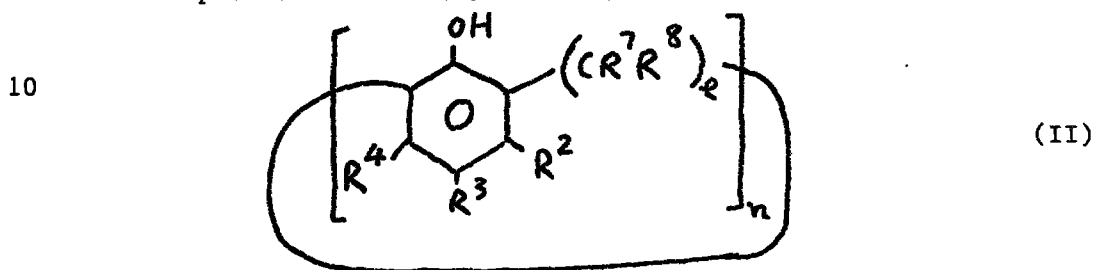
either R¹ is hydroxyl and R² and R⁴ are independently either hydrogen, hydrocarbyl or hetero-substituted hydrocarbyl, or R² and R⁴ are hydroxyl and R¹ is either hydrogen, hydrocarbyl or hetero-substituted hydrocarbyl; and



n is an integer in the range from 3 to 12.

In the formula (I), Y may suitably be $(CHR^6)_d$ in which R^6 either hydrogen or hydrocarbyl e.g. of 1-6 carbons such as methyl and d is an integer which is at least one, n preferably is from 4 to 9. Any hetero substituted hydrocarbyl group has the heteroatom preferably O or NH interrupting a chain of carbon atoms, such as an alkoxy-alkyl group of 2-20 carbons.

A preferred calixarene has the formula:-



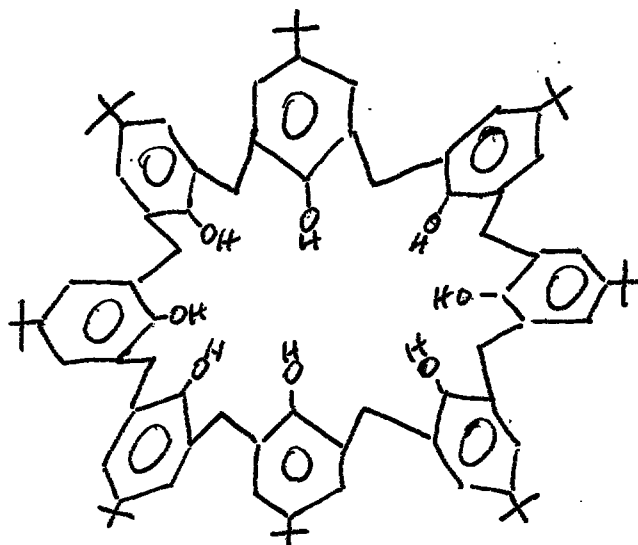
15 wherein R^2 , R^3 and R^4 are independently either hydrogen, hydrocarbyl or hetero-substituted hydrocarbyl, either one of R^7 and R^8 is hydrogen and the other is either hydrogen or hydrocarbyl, n is an integer in the range 4 to 9, and e is one or greater e.g. 1-4.

20 Preferably in the formula (II), R^2 and R^4 are hydrogen, R^3 is hydrocarbyl e.g. of 1-20 such as 3-16 carbon atoms or hetero-substituted hydrocarbyl, more preferably alkyl, one of R^7 or R^8 is hydrogen and the other is either hydrogen or alkyl, n is either 4, 6 or 8 and e is one. In the case where one of R^7 or R^8 is alkyl, it is preferably C_1 - C_4 alkyl, more preferably methyl. Preferably R^3 is alkyl, in particular nonyl (or a propylene trimer), t-butyl, dodecyl or tertiary-amyl. p-Alkylcalixarenes are also known as p-alkylphenol calixarenes and both terms will be used herein. An example of a suitable calixarene of the formula (II) is

30 p-tert-butyl calix [6,8] arene. The [8] arene, for example, may be represented by the formula:-



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Other suitable calixarenes include p-dodecyl calix[6]arene, p-nonyl calix[8]arene and p-nonyl[6,7,8]arene.

Calixarenes may suitably be prepared by the method described in the aforesaid Monograph, Chapter 2. Typically, an alkyl phenol unsubstituted at the ortho-positions may be reacted in the presence of a base with an aldehyde, such as formaldehyde or acetaldehyde.

The metal moiety of the salts may suitably be either an alkali or an alkaline earth metal, or indeed any metal capable of forming salts with calixarenes. Preferred metals include calcium, magnesium or barium. A particularly preferred metal is calcium. The salts, will hereinafter be termed "calixarates". Overbased calixarates, the subject of the present invention, are calixarates in which the ratio of the number of equivalents of the metal moiety to the number of equivalents of the acid moiety is greater than one.

In another aspect the present invention provides a process for the production of an overbased calixarate as hereinbefore described which process comprises reacting at elevated temperature:-

- (A) either (i) a sulphur-free calixarene having a substituent hydroxyl group or groups available for reaction with metal base, (ii) a low-based metal calixarate, (iii) a neutral metal calixarate or (iv) an overbased metal calixarate,
- (B) a metal base added either in a single addition or in a plurality of additions at intermediate points during the reaction,

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(C) A solvent comprising either:-

(C₁) either (i) a polyhydric alcohol having 2 to 4 carbon atoms, (ii) a di- (C₃ or C₄) glycol, (iii) a tri- (C₂-C₄) glycol or (iv) a mono- or poly-alkylene glycol alkyl ether of the formula:



wherein in the formula (III) R⁹ is a C₁ to C₆ alkyl group, R¹⁰ is an alkylene group e.g. 1-6 or 2-4 carbon atoms, R¹¹ is hydrogen or a C₁ to C₆ alkyl group and f is an integer from 1 to 6,

either alone or in combination with either (C₂) a hydrocarbon solvent or (C₃) either (i) water, (ii) a C₁ to C₂₀ monohydric alcohol, (iii) a C₁ to C₂₀ ketone, (iv) a C₁ to C₁₀ carboxylic acid ester or (v) an aliphatic, alicyclic or aromatic C₁ to C₂₀ ether, or,

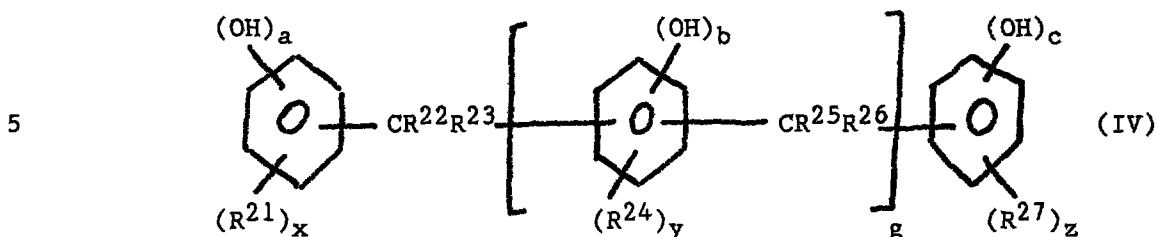
(C₄) a C₁ to C₄ monohydric alcohol, in combination with a hydrocarbon solvent (C₂), and

(D) carbon dioxide added subsequent to each addition of component (B).

With regard to component (A) this may be either (i) a sulphur-free calixarene having a substituent hydroxyl group or groups available for reaction with metal base, (ii) a low-based calixarate, (iii) a neutral calixarate or (iv) an overbased calixarate. Suitable calixarenes (i) are those as hereinbefore described, particularly those alkyl calixarenes capable of conferring oil-solubility on the product. Preferred calixarenes include p-tert-butyl calix[6,8]arene, p-dodecyl calix[6]arene, p-nonyl calix[8]arene and p-nonyl calix[6,7,8]arene. Pre-formed calixarates wherein the equivalent ratio of metal base moiety to calixarene is either 1 (neutral calixarates) or less than 1 (low-based calixarates) may be employed to produce an overbased calixarate. Alternatively, an overbased calixarate according to the present invention may be employed, in which case the product is a calixarate having an increased degree of overbasing, i.e. a higher alkalinity value.



In addition to one of the alternatives (i) to (iv), component (A) may further include a compound of the general formula:-



wherein a, b and c each independently represent 1 or 2;

x, y and z each independently represent zero or an integer from 1 to 3;

R²¹, R²⁴ and R²⁷ independently represent either hydrogen or a hydrocarbyl group, when x, y or z is greater than 1, each R²¹, each R²⁴ or each R²⁷ respectively being the same or different;

R²², R²³, R²⁵ and R²⁶ independently represent hydrogen or an alkyl group; and

g is an integer from 1 to 20.

Preferred compounds of the formula (IV) are those in which a, b and c are 1; x, y and z are 1; R²¹, R²⁴ and R²⁷ is preferably a C₁ to C₂₄ alkyl group, more preferably a C₁-C₁₂ alkyl group; either R²²=R²³=R²⁵=R²⁶= hydrogen or R²²=R²⁵= hydrogen and R²³=R²⁶= methyl; and g is preferably from 2 to 7, more preferably 3, Where R²², R²³, R²⁵ and R²⁶ all represent hydrogen, the compound of general formula (IV) can be prepared by the condensation of the corresponding phenol with formaldehyde. Where one of R²² and R²³ and one of R²⁵ and R²⁶ is hydrogen and the other is a hydrocarbyl group, for example a lower alkyl group, an aldehyde other than formaldehyde is used in the condensation with the phenol. Compounds of the formula (IV) are described in our copending UK application No.9013317.4 (BP Case No.7509) in relation to their alkali or alkali metal salts. The mixture of overbased salts and any low-based, neutral or unreacted compounds resulting from the use of the mixed feed is useful as a lubricating oil additive.

Component (B) is a metal base. The metal moiety may suitably be an alkali or alkaline earth metal, preferably an alkaline earth metal. The alkaline earth metal is preferably calcium, magnesium or



barium, more preferably calcium. The base moiety may suitably be an oxide or a hydroxide, preferably the hydroxide. A calcium base may be added, for example, in the form of quick lime (CaO) or in the form of slaked lime (Ca(OH)₂) or mixtures of the two in any
5 proportions. Component (B) may be added in whole to the initial reactants or in part to the initial reactants and the remainder in one or more further additions at intermediate points during the reaction.

Component (C) is a solvent for the reactants. The solvent (C)
10 may be either (C₁) either alone or in combination with either (C₂) or (C₃), or the solvent (C) may be (C₄) in combination with (C₂) wherein:

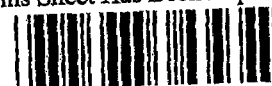
- (C₁) is either (i) a polyhydric alcohol having 2 to 4 carbon atoms,
(ii) a di-(C₃ or C₄) glycol, (iii) a tri-(C₂ to C₄) glycol or
15 (iv) a mono- or poly-alkylene glycol alkyl ether of the formula:-



wherein in the formula (III) R⁹ is a C₁ to C₆ alkyl group, R¹⁰ is an alkylene group, R¹¹ is hydrogen or a C₁ to C₆ alkyl group and f is an integer from 1 to 6. Suitable compounds having the formula (III)
20 include the monomethyl or dimethyl ethers of (a) ethylene glycol, (b) diethylene glycol, (c) triethylene glycol or (d) tetraethylene glycol. A suitable compound is methyl diglycol (CH₃OCH₂CH₂OCH₂CH₂OH). Mixtures of glycol ethers of formula (V) and glycols may also be employed. The polyhydric alcohol may suitably
25 be either a dihydric alcohol, for example ethylene glycol or propylene glycol, or a trihydric alcohol, for example glycerol. The di-(C₃ or C₄) glycol may suitably be dipropylene glycol, the tri-(C₂ to C₄) glycol may suitably be triethylene glycol. Preferably the component (C₁) is either ethylene glycol or methyl diglycol.

30 (C₂) is a hydrocarbon solvent which may be aliphatic or aromatic. Examples of suitable hydrocarbons include toluene, xylene, naphtha and aliphatic paraffins, for example hexane, and cycloaliphatic paraffins.

(C₃) may be either (i) water, (ii) a C₁ to C₂₀ monohydric
35 alcohol, (iii) a C₁ to C₂₀ ketone, (iv) a C₁ to C₁₀ carboxylic acid



ester or (v) an aliphatic, alicyclic or aromatic C₁ to C₂₀ ether. Examples are methanol, 2-ethyl hexanol, cyclohexanol, cyclohexanone, benzyl alcohol, ethyl acetate and acetophenone.

(C₄) may be a C₁ to C₄ monohydric alcohol, preferably methanol.

5 Preferred solvents (C) comprise ethylene glycol, a mixture of ethylene glycol and 2-ethyl hexanol and a mixture of methanol and toluene.

Generally, in view of the intended use of the product, it is preferred to incorporate a lubricating oil as a solvent. The
10 lubricating oil may suitably be an animal, a vegetable or a mineral oil. Suitably the lubricating oil is a petroleum - derived lubricating oil, such as a naphthenic base, paraffin i.e. base or mixed base oil. Solvent neutral oils are particularly suitable. Alternatively, the lubricating oil may be a synthetic lubricating
15 oil. Suitable synthetic lubricating oils include synthetic ester lubricating oils, which oils include diesters such as di-octyl adipate, di-octyl sebacate and tri-decyladipate, or polymeric hydrocarbon lubricating oils, for example liquid polyisobutenes and poly-alpha olefins.

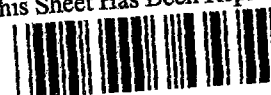
20 Component (D) is carbon dioxide, added subsequent to each addition of component (B). Carbon dioxide may be added in the form of a gas or a solid, preferably in the form of a gas. In gaseous form it may suitably be blown through the reaction mixture.

Preferably the reaction mixture may additionally incorporate as
25 Component (E) either (i) a C₆ to C₁₀₀ carboxylic acid or an anhydride thereof, (ii) a di- or polycarboxylic acid containing from 36 to 100 carbon atoms or an anhydride thereof, (iii) a hydrocarbyl-substituted sulphonic acid or anhydride thereof, (iv) a hydrocarbyl-substituted salicylic acid or anhydride thereof, (v) a
30 hydrocarbyl-substituted naphthenic acid or anhydride thereof, (vi) a hydrocarbyl-substituted phenol or (vii) a mixture of any two or more of (i) to (vi), of which (i) is preferred.

As regards (i), this is preferably an acid having the formula:



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wherein R^{12} is a C_{10} to C_{24} alkyl or alkenyl group and R^{13} is either hydrogen, a C_1 to C_4 alkyl group or a $-CH_2COOH$ group. Preferably R^{12} in the formula is an unbranched alkyl or alkenyl group.

Preferred acids of formula (V) are those wherein R^{13} is hydrogen and
5 R^{12} is a C_{10} to C_{24} , more preferably C_{18} to C_{24} unbranched alkyl group. Examples of suitable saturated carboxylic acids of formula (V) include capric, lauric, myristic, palmitic, stearic, isostearic, arachidic, behenic and lignoceric acids. Examples of suitable
10 unsaturated acids of formula (V) include lauroleic, myristoleic, palmitoleic, oleic, gadoleic, erucic, ricinoleic, linoleic and linolenic acids. Mixtures of acids may also be employed, for example rape top fatty acids. Particularly suitable mixtures of acids are those commercial grades containing a range of acids, including both saturated and unsaturated acids. Such mixtures may
15 be obtained synthetically or may be derived from natural products, for example tall, cotton, ground nut, coconut, linseed, palm kernel, olive, palm, castor, soyabean, sunflower, herring and sardine oils and tallow.

Instead of, or in addition to, the carboxylic acid there may be
20 used the acid anhydride, the acid chloride or the ester derivatives of the acid, preferably the acid anhydride. It is preferred however to use a carboxylic acid or a mixture of carboxylic acids. A preferred carboxylic acid of formula (V) is stearic acid. The acid may suitably be present in an amount up to 40%w/w, based on the
25 total weight of the final product. It is believed that the acid, when present, chemically modifies the overbased calixarate product.

As regards (ii), this is preferably a polyisobutene succinic acid or a polyisobutene succinic anhydride.

As regards the hydrocarbyl substituent of (iii), (iv), (v) and
30 (vi), this may suitably contain up to 125 aliphatic carbon atoms. Examples of suitable substituents include alkyl radicals, for example hexyl, cyclohexyl, octyl, isoctyl, decyl, tridecyl, hexadecyl, eicosyl and tricosyl, radicals derived from the polymerisation of both terminal and internal olefins, for example
35 ethene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-butene,



2-pentene, 3-pentene and 4-octene. Preferably the hydrocarbonyl substituent is one derived from a polypropylene, poly-1-butene or polyisobutene.

The reaction mixture may also incorporate as component (F) a catalyst (or promoter) for the reaction. The catalyst may be an organic compound or an inorganic compound. Suitable organic compounds include (i) organic halides or (ii) organic alkanoates, which may suitably be represented by the formula:-



wherein in the formula (VI) X is either halogen, suitably chlorine, bromine or iodine, preferably chlorine, or the group $OCOR^{15}$ wherein R^{15} is suitably C_1 to C_4 alkyl and R^{14} is either an alkyl, aryl or alkaryl group preferably having 3-20 or 6-20 or 7-20 carbons respectively, or halo-derivative thereof. Alternatively, the organic halide may be an HX salt of an organic base, for example guanidine hydrochloride. A suitable example of an organic halide of the formula (VI) is octyl chloride. Mixtures of (i) and (ii) may also be employed. Suitably the amount of organic compound (F) employed may be up to 2.0% by weight based on the weight of concentrate. Suitable inorganic compound catalysts include inorganic halides, particularly inorganic chlorides, and inorganic alkanoates. Examples of suitable inorganic compound catalysts include calcium acetate, calcium chloride, ammonium chloride, aluminium chloride and zinc chloride, of which calcium chloride and calcium acetate are preferred. Suitably the amounts of the inorganic compound catalyst employed may be up to 2.0% wt/wt based on the weight of the reaction mixture. Provided that the catalyst is present during the carbonation step, it may be added at any point in the process, though it will usually be found convenient to add the catalyst initially.

In order to produce an overbased calixarate from component (A)(i), (A)(ii) or (A)(iii) it is necessary only to react the (A) component with components (B), (C) and (D), using the appropriate proportions of components (A) and (B) to achieve overbasing. Suitably component (B) may be added in one or more additions,



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preferably in a single addition.

In order to produce a high TBN (Total Base Number) overbased calixarate, as an alternative to components (A)(i) to (iii) component (A)(iv) may be employed, and it is preferred to employ
5 component (E), particularly either (E)(i) or (ii) and more particularly stearic acid, whilst at the same time adjusting the relative amounts of components (A) and (B) to a value sufficient to produce the high TBN desired. Again, component (B) may suitably be incorporated in one or more additions, preferably in a single
10 addition.

Suitably the elevated temperature at which the process is operated may be a temperature in the range from 15 to 200°C, preferably from 50 to 175°C. The selection of the optimum temperature within the aforesaid range will depend to a large extent
15 on the nature of the solvent employed.

Generally, the process will be operated in the presence of a lubricating oil. At the conclusion of the process it is preferred to recover the salt as a solution in lubricating oil by separating off volatile fractions, for example by distillation at
20 subatmospheric pressure.

Finally, it is preferred to filter the solution. Alternatively, the solution may be centrifuged.

In another aspect the present invention also provides a composition suitable for use as an additive to lubricating oils
25 which composition comprises as a first component an overbased calixarate as hereinbefore described and as a second component a neutral and/or an overbased metal salt of at least one of
(i) a C₆ to C₁₀₀ carboxylic acid,
(ii) a di- or polycarboxylic acid containing from 36 to 100 carbon
30 atoms,
(iii) a hydrocarbyl-substituted sulphonic acid,
(iv) a hydrocarbyl-substituted salicylic acid,
(v) a hydrocarbyl-substituted naphthenic acid or
(vi) a hydrocarbyl-substituted phenol.

35 Suitably the metal moiety of the salts in the composition may



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be either an alkali or an alkaline earth metal, preferably an alkaline earth metal, more preferably calcium, magnesium or barium.

The composition may be prepared simply by mixing the components. Preferably, however the composition is prepared by
5 reacting components (A), (B), (C), (D) and (E), and optionally (F).

The overbased calixarates of the invention are useful in lubricating oil compositions both for their acids neutralisation capability and their detergent and antioxidant properties.

In a final aspect the present invention provides a finished
10 lubricating oil composition which composition comprises a lubricating oil usually in a major proportion and an overbased alkaline earth metal salt of a calixarene as hereinbefore described, usually in a minor proportion; amounts of the calixarene salt may be 0.01-50% e.g. 0.1-35% by weight of the composition.

15 The finished lubricating oil composition may also contain effective amounts of one or more other types of conventional lubricating oil additives, for example viscosity index improvers, anti-wear agents, antioxidants, dispersants, rust inhibitors, pour-point depressants, or the like, which may be incorporated into
20 the finished lubricating oil composition either directly or through the intermediacy of a concentrate composition.

The invention will now be further illustrated by reference to the following Examples. In all the Examples the term AV (Alkalinity Value) is used. AV is expressed in terms of mg KOH/g as measured by
25 ASTM D2896. In the Examples where lime is used, it is in the form of slaked lime, Ca(OH)_2 . Viscosities were measured by the method of ASTM D445.

Example 1

<u>Initial charge</u>	-	p-t-Butyl Calix [6,8] arene	75g
30		Lubricating oil	131g
		2-Ethylhexanol	224g
		Stearic acid	70g
		Calcium chloride	4g

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Method

- (i) The initial charge was heated to 125°C and lime (53g) was charged,
(ii) the temperature was increased to 145°C. Ethylene glycol
5 (36g) was charged whilst ramping the temperature to 165°C,
(iii) the mixture was held at 165°C for 1 hour,
(iv) carbon dioxide (40g) was added at 165°C/1 bar,
(v) the mixture was stripped at 200°C/10mm Hg, and
(vi) the product was filtered through filteraid.

10 RESULTS

Product weight = 340g

Distillate weight = 232g

Product Composition After Filtration

Ca = 8.8%

15 Ca incorporation efficiency = 99.5%

AV = 233mg KOH/g

CO₂ = 7.6%

Viscosity at 100°C = 109cSt

Examples 2 to 5

20 The procedure of Example 1 was repeated.

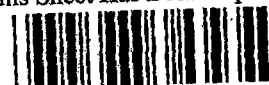
The reactants, their relative proportions and the results obtained for Examples 1 to 5 are given in the accompanying Table 1.

Example 6

	<u>Initial charge</u>	-	p-t-Butyl Calix [6,8] arene	110g
25			Lubricating oil	131g
			2-Ethylhexanol	40g
			Stearic acid	35g
			Calcium chloride	4g
			Toluene	200g
30			Methanol	20g

Method

- (i) The charge was heated to 60°C and lime (76g) was added,
(ii) the mixture was held at 60°C for 1 hour,
(iii) carbon dioxide (57g) was added at 60°C/1 bar,
35 (iv) methanol (10g) and lime (35g) were added at 60°C,



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- (v) the mixture was held at 60°C for 1 hour,
- (vi) carbon dioxide (30g) was added at 60°C/1 bar,
- (vii) the mixture was stripped at 160°C/10mm Hg, and
- (viii) the product was filtered through filteraid.

5 RESULTS

Product weight = 417g

Product Composition After Filtration

Ca = 10.6%
Ca incorporation efficiency = 71.9%
10 AV = 290mg KOH/g
CO₂ = 6.8%
Viscosity at 100°C = 143cSt

Example 7

The procedure of Example 6 was repeated.

- 15 The reactants, their relative proportions and the results obtained are given in the accompanying Table 1.

Comparison Test

The procedure of Example 6 was repeated except that the calixarene was omitted from the initial charge.

- 20 The reactants their relative proportions and the results obtained for Examples 6 and 7 are given in the accompanying Table 1.

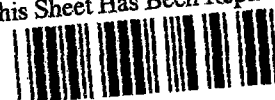
Example 8

Initial charge - p-t-Butyl Calix [6,8] arene 75g
Lubricating oil 131g
25 2-Ethylhexanol 224g

Method

- i) The initial charge was heated to 125°C and lime (56g) was charged,
- ii) The temperature was increased to 145°C. Stearic acid (70g)
30 was charged,
- iii) Ethylene glycol (36g) was charged whilst ramping the temperature to 165°C,
- iv) The mixture was held at 165°C for 1 hr.,
- v) Carbon dioxide (55g) was added at 165°C/1 bar,
- 35 vi) The mixture was stripped at 200°C/10mm Hg, and

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vii) The product was filtered through filteraid.

RESULTS

Product weight = 338g

Product Composition After Filtration

5 Ca = 8.6%
Ca incorporation efficiency = 96%
AV = 242mg KOH/g
Viscosity at 100°C = 454cSt

Example 9

10 The procedure of Example 8 was repeated. The reactants, their relative proportions and the results obtained are given in the accompanying Table 1.

Examples 10 - 11

The procedure of Example 8 was repeated except that p-Nonyl
15 Calix [6,7,8] arene was used in place of p-t-butyl Calix [6,8] arene. The reactants, their relative proportions and the results obtained are given in the accompanying Table 1.

Examples 12-30

Nonylphenolcalix(6,8)arene in xylene solution (330g of 13.64%
20 solution, 0.03 moles) and SN150 diluent oil (90g) were charged to a 1 litre, 5 necked, round bottomed, flange flask with take off condenser, thermopocket (with thermometer and thermocouple) and agitator (paddle type). The temperature of the mixture was raised to 110°C and vacuum (29''Hg) applied to distil off the xylene. The
25 vacuum was removed and while maintaining the temperature between 100 and 110°C, 2-ethylhexanol (222g, 1.7 moles) was added, with stirring at approximately 500rpm. The reaction mixture was raised to 130°C and lime (58g, 0.78 moles) was added over 5 minutes. Vacuum
(10''Hg) was applied to the reactor and held for 15 minutes at
30 130°C. The vacuum was removed and stearic acid (100g, 0.35 moles) was added over 10 minutes and vacuum (10''Hg) was reapplied to the reactor and held for 15 minutes at 130°C. The vacuum was removed and ethylene glycol (36g, 0.58 moles) was added over 15 minutes and vacuum (10''Hg) was reapplied and the reaction held at 130°C for 60
35 minutes. The vacuum was removed and CO₂(58g, 1.3 moles) was added



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over approximately 30-40 minutes. Vacuum (29"Hg) was applied and the temperature raised to 200°C. After 90 minutes, the vacuum was removed and the product cooled to 140°C. The product was filtered through a 15mm deep pad of compressed clarcel DIC filter aid, supported on a no.1 glass sinter funnel.

The batches of nonyl calixarate listed in Table 2 were manufactured in a similar manner as outlined above, however there are changes of conditions i.e. temperature, glycol and stearic acid. These are listed in Table 2.

10 Examples 31-37

Nonylphenolcalix(6,8)arene in xylene solution (330g of 13.64% solution, 0.03 moles) and alkyl phenol with SN150 diluent oil (90g) were charged to a 1 litre, 5 necked, round bottomed, flange flask with take off condenser, thermopocket (with thermometer and thermocouple) and agitator (paddle type). The temperature of the mixture was raised to 110°C and vacuum (29"Hg) applied to distil off the xylene. The vacuum was removed and while maintaining the temperature between 100 and 110°C, 2-ethylhexanol (222g, 1.7 moles) was added, with stirring at approximately 500 rpm. The reaction mixture was raised to 130°C and lime (58g 0.78 moles) was added over 5 minutes. Vacuum (10"Hg) was applied to the reactor and held for 15 minutes at 130°C. The vacuum was removed and stearic acid (100g 0.35 moles) was added over 10 minutes and vacuum (10"Hg) was reapplied to the reactor and held for 15 minutes at 130°C. The vacuum was removed and ethylene glycol (36g, 0.58 moles) was added over 15 minutes and vacuum (10"Hg) was reapplied and the reaction held at 130°C for 60 minutes. The vacuum was removed and CO₂ (58g, 1.3 moles) was added over approximately 30-40 minutes. Vacuum (29"Hg) was applied and the temperature raised to 200°C. After 90 minutes, the vacuum was removed and the product cooled to 140°C. The product was filtered through a 15mm deep pad of compressed Clarcel DIC filter aid, supported on a No 1 glass sinter funnel.

The batches of nonyl calixarate listed in Table 3 were manufactured in a similar manner as outlined above, however there are changes in the alkyl phenol used ie type or amount. These are

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listed in Table 3.

Examples 38-45

The alkyl calixarene in xylene solution (330g of 13.64% solution, 0.03 moles) with SN150 diluent oil (90g) were charged to a 1 litre, 5 necked, round bottomed, flange flask with take off condenser, thermopocket (with thermometer and thermocouple) and agitator (paddle type). The temperature of the mixture was raised to 110°C and vacuum (29"Hg) applied to distil off the xylene. The vacuum was removed and while maintaining the temperature between 100 and 110°C, 2-ethylhexanol (222g, 1.7 moles) was added, with stirring at approximately 500 rpm. The reaction mixture was raised to 130°C and lime (58g, 0.78 moles) was added over 5 minutes. Vacuum (10"Hg) was applied to the reactor and held for 15 minutes at 130°C. The vacuum was removed and stearic acid (100g, 0.35 moles) was added over 10 minutes and vacuum (10"Hg) was reapplied to the reactor and held for 15 minutes at 130°C. The vacuum was removed and ethylene glycol (36g 0.58 moles) was added over 15 minutes and vacuum (10"Hg) was reapplied and the reaction held at 130°C for 60 minutes. The vacuum was removed and CO2 (58g, 1.3 moles) was added over approximately 30-40 minutes. Vacuum (29"Hg) was applied and the temperature raised to 200°C. After 90 minutes, the vacuum was removed and the product cooled to 140°C. The product was filtered through a 15mm deep pad of compressed Clarcel DIC filter aid, supported on a No 1 glass sinter funnel.

The batches of alkyl calixarate listed in Tables 4 and 5 were manufactured in a similar manner as outlined above, however there are changes in the alkyl phenol and temperature of reaction used. These are listed in Tables 4 and 5.

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TABLE 1

Example	Carbon- ation Temp. (°C)	REACTANTS					PRODUCT				
		Calix arene (g)	Stearic acid (g)	Catalyst	Lime (g)	CO ₂ (g)	Filtration Rate	% Ca w/w	AV mgKOH/g	Viscosity at 100°C (cSt)	%CIE
1	165	75	70	Solid CaCl ₂	53	40	A	8.8	233	109	99.5
2	165	75	70	Solid CaCl ₂	53	26	B	-	240	-	-
3	165	110	35	Solid CaCl ₂	76	57	C	11.3	298	-	96.7
4	165	95	50	Solid CaCl ₂	76	61	C	11.8	320	-	95+
5	165	75	70	Solid CaCl ₂	56	63	A	9.1	251	140	97
6	60	110	35	Solid CaCl ₂	111	87	B	10.6	290	143	71.9
7	60	110	35	Solid CaCl ₂	76	57	A	7.0	189	195	59.4
8	165	75	70	No Catalyst	56	55	A	8.6	242	454	96
9	165	45	100	No Catalyst	56	55	A	9.0	258	278	94
10	165	45	100	No Catalyst	56	55	A	8.4	247	51	87
11	165	45	100	No Catalyst	85	85	A	11.5	363	171	72
CT	165	0	145	No Catalyst	56	55	A	9.2	248	*	

AbbreviationsCT = Comparison TestFiltration Rate

A = Acceptable; B = Difficult

C = Dilution with toluene prior to filtration necessary

CIE = Calcium incorporation efficiency

AV = Alkalinity Value

* Product solidified on standing



TABLE 2

EXAMPLE	TEMP. (°C)	GLYCOL (g)	STEARIC ACID(g)	CALIXARENE (g)	SN150 (g)	Ca (%)	V100 (Cst)
12	130	36	100	330	90	9.86	173.4
13	130	36	80	330	90	10.47	153.6
14	110	36	100	330	90	10.04	182.2
15	110	36	80	330	90	10.48	90.3
16	130	30	100	330	90	8.56	139.2
17	130	30	80	330	90	8.68	94.1
18	110	30	100	330	90	11.13	268.6
19	110	30	80	330	90	10.86	130.9
20	130	36	100	264	90	10.49	138.8
21	130	36	80	264	90	10.47	145.8
22	110	36	100	264	90	11.34	104.7
23	110	36	80	264	90	11.27	126.7
24	130	30	100	264	90	10.56	163.1
25	130	30	80	264	90	10.92	151.7
26	110	30	100	264	90	11.26	155.0
27	110	30	80	264	90	11.95	-
28	130	36	80	330	90	10.84	162.3
29	130	36	80	363	90	11.19	130.2
30	130	36	60	363	130	8.86	63.6

NOTE

- 1) The change in temperature applies to every part of the reaction procedure from the addition of lime to the carbonation stage.
- 2) 36g of glycol = 0.58 moles
30g of glycol = 0.48 moles
- 3) 100g of stearic acid = 0.35 moles
80g of stearic acid = 0.28 moles
60g of stearic acid = 0.21 moles
- 4) 363g of nonylphenolcalix(6,8)arene = 0.033 moles
264g of nonylphenolcalix(6,8)arene = 0.024 moles



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Table 3

Ex	Alkyl	Phenol (g)	Calixarene (g)	SN150 (g)	Ca (%)	V100 (Cst)
	DDP	NP				
31	4.5	-	330	90	9.58	125.7
32	9.0	-	264	90	9.98	118.8
33	-	9.0	264	90	9.55	167.1
34	-	9.0	264	90	10.09	147.6
35	9.0	-	264	90	10.58	225.5
36	9.0	-	264	90	11.40	104.4
37	9.0	-	330	110	9.63	97.6

NOTE

1. DDP = Dodecylphenol
2. NP = Nonylphenol
3. 330g of nonylphenolcalix (6,8)arene = 0.030 moles
4. 264g of nonylphenolcalix (6,8)arene = 0.024 moles

Table 4

Prep No	Alkyl Calixarene	(g)	Temperature (°C)	SN150 (g)	Ca (%)	V100 (Cst)
38	AMYL	52.5	130	90	10.67	122.2
39	p-DODECYL	330	110	110	9.79	65.7
40	p-DODECYL	330	130	110	10.29	67.8

NOTE

1. 52.5g of amyl phenolcalixarene (65% solution in petroleum distillate) = 0.03 moles
2. 330g of p-dodecylphenolcalixarene = 0.03 moles

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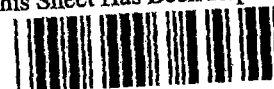
Table 5

Prep No	Alkyl Calixarene	(g)	Temperature (°C)	SN150 (g)	Ca (%)	V100 (Cst)
41	A	62.5	130	90	7.58	189.1
42	B	330	130	90	9.41	133.9
43	B	330	110	110	8.73	62.5
44	B	330	130	110	9.76	67.8
45	C	90	130	90	9.86	89.9

NOTE

1. 'A' is a mixture of t-butyl phenolcalixarene/t-butyl phenol formaldehyde resin/free t-butyl phenol (50% solution in xylene) = 0.03 moles.
2. 'B' is an alkyl phenolcalixarene made from alkyl phenol which contains about 65% of the para isomer and the alkyl group is dodecyl (13.64% solution in xylene) = 0.03 moles.
3. 'C' is a mixture of p-nonyl phenolcalixarene/p-nonyl phenol formaldehyde resin/free p-nonyl phenol (50% solution in xylene) = 0.03 moles.

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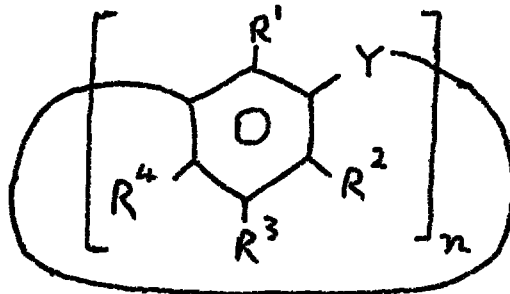
Case 7455(2)



Claims:

1. A non-sulphurised overbased metal salt of a sulphur-free calixarene having a substituent hydroxyl group or groups available for reaction with metal base.

2. An overbased metal salt according to claim 1 wherein the calixarene has the formula:



(I)

wherein in the formula (I):

Y is a divalent bridging group;

R³ is a hydrocarbyl or a hetero-substituted hydrocarbyl group;

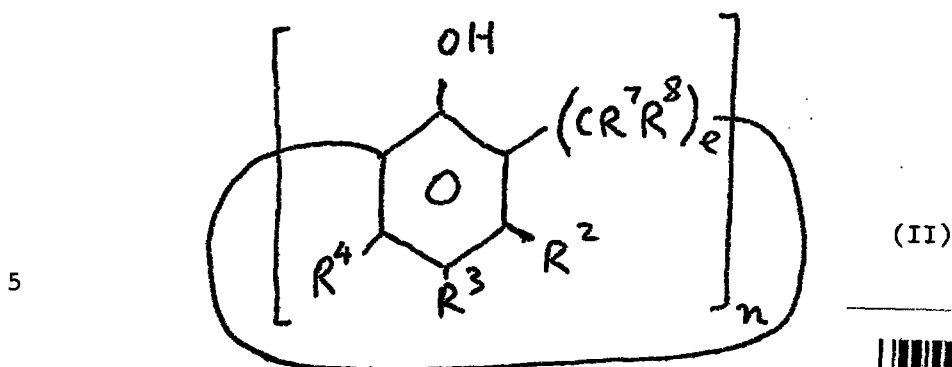
either R¹ is hydroxyl and R² and R⁴ are independently either hydrogen, hydrocarbyl or hetero-substituted hydrocarbyl or R² and R⁴ are hydroxyl and R¹ is either hydrogen, hydrocarbyl or hetero-substituted hydrocarbyl; and

n is an integer in the range from 3 to 12.

3. An overbased metal salt according to claim 2 wherein n has a value in the range from 4 to 9 and the group Y is (CHR⁶)_d in which R⁶ is either hydrogen or hydrocarbyl and d is an integer which is at least one.

4. An overbased metal salt according to claim 1 wherein the calixarate has the formula:-





wherein in the formula (II):

10 R^2 , R^3 and R^4 are independently either hydrogen, hydrocarbyl, or hetero-substituted hydrocarbyl;

either one of R^7 and R^8 is hydrogen and the other is either hydrogen or hydrocarbyl;

n is an integer in the range 4 to 9; and e is one or greater.

15 5. An overbased metal salt according to claim 4 wherein in the formula (II):-

R^2 and R^4 are hydrogen;

R^3 is alkyl;

one of R^7 or R^8 is hydrogen and the other is either hydrogen or

20 alkyl; n is either 4, 6 or 8; and

e is one.

6. An overbased metal salt according to claim 5 wherein R^3 is either nonyl, t-butyl, dodecyl or tertiary-amyl.

7. An overbased metal salt of either p-tert-butyl calix, 25 [6,8]arene, p-dodecyl calix [6]arene, p-nonyl calix[8]arene or p-nonyl calix [6,7,8]arene.

8. An overbased metal salt according to any one of the previous claims wherein the metal moiety of the salt is either calcium magnesium or barium.

30 9. An overbased metal salt according to claim 8 wherein the metal moiety is calcium.

10. A process for the production of the overbased metal salt of claims 1 to 9 which process comprises reacting at elevated temperature:-

35 (A) either (i) a sulphur-free calixarene having a substituent





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hydroxyl group or groups available for reaction with metal base,
(ii) a low based metal calixarate, (iii) a neutral metal
calixarate or an overbased metal salt according to claim 1,

(B) a metal base added either in a single addition or in a
plurality of additions at intermediate points during the
reaction,

(C) A solvent comprising either:-

(C₁) either (i) a polyhydric alcohol having 2 to 4 carbon
atoms, (ii) a di- (C₃ or C₄) glycol, (iii) a tri- (C₂-C₄)
glycol or (iv) a mono- or poly-alkylene glycol alkyl ether of
the formula:



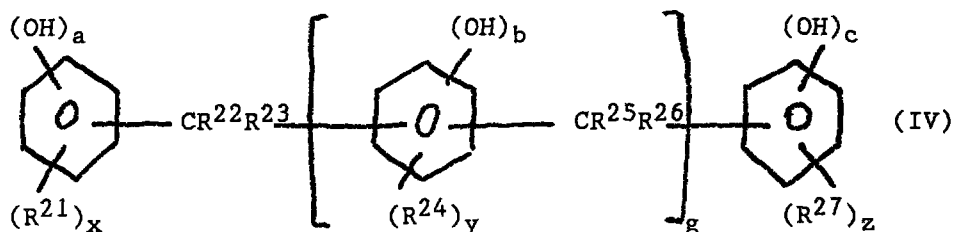
wherein in the formula (III) R⁹ is a C₁ to C₆ alkyl group, R¹⁰
is an alkylene group, R¹¹ is hydrogen or a C₁ to C₆ alkyl group
and f is an integer from 1 to 6,

either alone or in combination with either (C₂) a hydrocarbon
solvent or (C₃) either (i) water, (ii) a C₁ to C₂₀ monohydric
alcohol, (iii) a C₁ to C₂₀ ketone, (iv) a C₁ to C₁₀ carboxylic
acid ester or (v) an aliphatic, alicyclic or aromatic C₁ to C₂₀
ether, or,

(C₄) a C₁ to C₄ monohydric alcohol, in combination with a
hydrocarbon solvent (C₂), and

(D) carbon dioxide added subsequent to each addition of component
(B).

11. a process according to claim 10 wherein component (A) further
includes a compound of the general formula:-



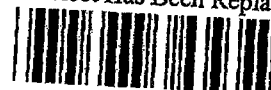
wherein in the formula (IV):-

a, b and c each independently represent 1 or 2;

x, y and z each independently represent zero or an integer from
1 to 3;

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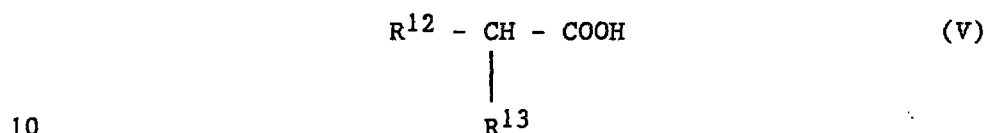
- 5 R^{21} , R^{24} and R^{27} independently represent either hydrogen or a hydrocarbyl group when x, y or z is greater than 1, each R^{21} each R^{24} or each R^{27} respectively being the same or different; R^{22} , R^{23} , R^{25} and R^{26} independently represent hydrogen or an alkyl group; and
- g is an integer from 1 to 20.
12. A process according to claim 11 wherein the compound of the formula (IV) is one in which:-
- a, b and c = 1;
- 10 x, y and z = 1;
- R^{21} , R^{24} and R^{27} is a C_1 - C_{12} alkyl group;
- either $R^{22} = R^{23} = R^{25} = R^{26} = H$ or $R^{22} = R^{25} = H$ and $R^{23} = R^{26} = CH_3$, and
- g = 2 to 7.
- 15 13. A process according to claim 10 wherein component (A) is a sulphur-free calixarene having a substituent hydroxyl group or groups available for reaction with metal base.
14. A process according to claim 10 wherein component (A) is an overbased metal salt according to claim 1.
- 20 15. A process according to any one of claims 10 to 14 wherein the metal base (B) is either quick lime (CaO) or slaked lime (Ca(OH)₂) or a mixture of the two in any proportions.
16. A process according to any one of claims 10 to 15 wherein the solvent (C) comprises ethylene glycol.
- 25 17. A process according to any one of claims 10 to 15 wherein the solvent (C) comprises a mixture of ethylene glycol and 2-ethyl hexanol.
18. A process according to any one of claims 10 to 15 wherein the solvent (C) comprises a mixture of methanol and toluene.
- 30 19. A process according to any one of claims 10 to 18 wherein the solvent (C) further incorporates a lubricating oil.
20. A process according to any one of claims 10 to 19 wherein the reaction mixture further incorporates component (E) which is either
- 35 (i) a C_6 to C_{100} carboxylic acid or an anhydride thereof, (ii) a di- or polycarboxylic acid containing from 36 to 100 carbon atoms or an





anhydride thereof, (iii) a hydrocarbyl-substituted sulphonic acid or
anhydride thereof, (iv) a hydrocarbyl-substituted salicylic acid or
anhydride thereof, (v) a hydrocarbyl-substituted naphthenic acid or
anhydride thereof, (vi) a hydrocarbyl-substituted phenol or (vii) a
5 mixture of any two or more of (i) to (vi).

21. A process according to claim 20 wherein component (E) is an
acid having the formula:-



wherein in the formula (V):

R^{12} is a C_{10} to C_{24} alkyl or alkenyl group; and R^{13} is either
hydrogen, a C_1 to C_4 alkyl group or a $-CH_2COOH$ group.

22. A process according to claim 21 wherein component (E) is
15 stearic acid.

23. A process according to any one of claims 10 to 22 wherein the
reaction mixture further incorporates component (F) which is a
catalyst (or promoter) for the reaction, which catalyst or promoter
is either calcium acetate or calcium chloride.

20 24. A composition suitable for use as an additive to lubricating
oils which composition comprises as a first component the overbased
metal salt of any of claims 1 to 9 or made by a process of any of
claims 10-23 and as a second component a neutral and/or an overbased
metal salt of at least one of (i) a C_6 to C_{100} carboxylic acid, (ii)
25 a di- or polycarboxylic acid containing from 36 to 100 carbon

atoms, (iii) a hydrocarbyl
substituted sulphonic acid, (iv) a hydrocarbyl-substituted salicylic
acid, (v) a hydrocarbyl-substituted naphthenic acid, or (vi) a
30 hydrocarbyl- substituted phenol.

25. A finished lubricating oil composition which composition
comprises a lubricating oil and a the overbased metal salt of any of
claims 1 to 9 or made by any of claims 10-23.

