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(54) **Sulphurised alkaline earth metal hydrocarbyl phenates, their production and use thereof**

Geschwefelt Erdalkalimetallalkylphenolate, ihre Herstellung und ihre Verwendung

Alkylphénates de métaux alcalino-terreux sulfurés, leur préparation et leur utilisation

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Description

[0001] The present invention relates in general to the production of sulphurised alkaline earth metal hydrocarbyl phenate additive concentrates and to their use as lubricating oil additives. In particular the present invention relates to the production of sulphurised alkaline earth metal hydrocarbyl phenate-containing additive concentrates having a high total base number (TBN) and an acceptable viscosity from sulphurised alkaline earth metal hydrocarbyl phenates having lower TBNs.

[0002] In the internal combustion engine, by-products from the combustion chamber often blow by the piston and admix with the lubricating oil. Many of these by-products form acidic materials within the lubricating oil. This is particularly marked in diesel engines operating on low-grade fuels of high sulphur content wherein corrosive acids are produced by combustion. The acids thereby incorporated in the lubricating oil can include sulphur acids produced by oxidation of sulphur, hydrohalic acids derived from halogen lead scavengers in the fuel and nitrogen acids produced by the oxidation of atmospheric nitrogen within the combustion chamber. Such acids cause deposition of sludge and corrosion of the bearings and engine parts leading to rapid wear and early breakdown of the engine.

[0003] One class of compounds generally employed to neutralise the acidic materials and disperse sludge within the lubricating oil are the sulphurised metal alkyl phenates, wherein the metal is an alkaline earth metal such as calcium, magnesium or barium. Both "normal" and "overbased" sulphurised alkaline earth metal alkyl phenates have been employed. The term "overbased" is used to describe those sulphurised alkaline earth metal alkyl phenates in which the ratio of the number of equivalents of the alkaline earth metal moiety to the number of equivalents of the phenol 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 phenol moiety in "normal" alkaline earth metal alkyl phenates is one. Thus, the "overbased" material contains greater than 20% in excess of the alkaline earth metal present in the corresponding "normal" material. For this reason "overbased" sulphurised alkaline earth metal alkyl phenates have a greater capability for neutralising acidic matter than do the corresponding "normal" alkaline earth metal alkyl phenates.

[0004] The prior art teaches many methods for preparing both "normal" and "overbased" sulphurised metal alkyl phenates. One such method for preparing "overbased" sulphurised alkyl phenates generally referred to as the "single lime addition" process comprises reacting an alkyl phenol, in the presence of lubricating oil, sulphur, a hydroxylic compound and excess alkaline earth metal hydroxide (above the stoichiometric proportion required to neutralise the alkyl phenol), to form an intermediate product, followed by carbonation, a heading distillation (to remove unreacted hydroxylic compound) and filtration. The production of intermediate product is accompanied by a marked increase in viscosity while the subsequent carbonation reduces the viscosity to a relatively low level. The increase in viscosity accompanying the formation of the intermediate product is undesirable because the reaction mixture becomes difficult to agitate to the detriment of subsequent reactions. Whilst this increase in viscosity may be controlled to an acceptable level by incorporation of less alkaline earth metal hydroxide in the reaction, the overbased alkyl phenate product necessarily possesses a reduced neutralisation capacity. In order to achieve a high neutralisation capacity product and at the same time control the viscosity of the intermediate product within acceptable limits the alkaline earth metal hydroxide may be added in two, (generally referred to as the "double lime addition" process) or three separate reaction steps, with sequential carbonation steps. However, this method involves relatively long batch times. Another alternative is to use viscosity depressants, such as tridecanol, 2-ethylhexanol, or similar boiling range hydroxylic solvent, in the production of the intermediate product but such an expedient increases the raw material cost of the process. The highest total base number (TBN), as measured in mg KOH/g, consistent with an acceptable viscosity, generally achievable by prior art processes is about 300, though generally prior art TBNs are in the range from 200-300. It would clearly be a desirable objective to produce sulphurised alkaline earth metal alkyl phenate compositions having a high TBN that is a TBN greater than 300, and preferably greater than 350. It would also be a desirable objective to produce such materials from sulphurised alkaline earth metal alkyl phenates having a lower TBN. To date it has not been found possible to achieve products of such high TBN because the use of larger concentrations of alkaline earth metal base leads to highly viscous products which, rather than being 'thinned' by subsequent carbonation attemps using excess carbon dioxide, are rendered insoluble. We have achieved these objectives and thereby achieved compositions having a TBN in excess of 300 and in some cases greater than 350 whilst retaining an acceptable viscosity, that is a viscosity of less than 1000 cSt, and avoiding insolubility by incorporating into a reaction mixture containing a sulphurised alkaline earth metal alkyl phenate at least one carboxylic acid or acid derivative thereof having at least 10 carbon atoms in the molecule.

[0005] The use of carboxylic acids in the production of sulphurised alkaline earth metal alkyl phenates is not new, see for example US-A-4049560 and EP-A-0094814.

[0006] US-A-4049560 describes the production of an overbased magnesium detergent by a process in which carbon dioxide is introduced into a reaction mixture which comprises:

(a) 15-40 wt % of a sulphurised phenol or thiophenol containing one or more hydrocarbyl substituents, or a phenol

or thiophenol containing one or more hydrocarbyl substituents, or said phenol or thiophenol containing one or more hydrocarbyl substituents together with sulphur,
(b) 5-15 wt % of an organic sulphonic acid, an organic sulphonate or an organic sulphate,
(c) 5-15 wt % of a glycol, a C_1 to C_5 monohydric alkanol or C_2 to C_4 alkoxy alkanol,
(d) 2-15 wt % of a magnesium hydroxide or active magnesium oxide,
(e) at least 0.1 wt % of a C_1 to C_{18} carboxylic acid, and
(f) at least 10% by weight of a diluent oil (including any present in components (a) and (b).

[0007] The amount of carboxylic acid (component (e)) is preferably in the range 0.5 to 2.0% by weight. The product prepared by this reaction is said to have a TBN of about 200 to 250, e.g. about 225.

[0008] EP-A-0094814 discloses an additive concentrate for incorporation in a lubricating oil composition comprising lubricating oil, and from 10 to 90 wt % of an overbased alkaline earth metal hydrocarbyl sulphurised phenate which has been treated, either during or subsequent to the overbasing process, with from 0.1 to 10, preferably 2 to 6, wt % (based on the weight of additive concentrate) of an acid of the formula:

(I)

(wherein R is a C_{10} to C_{24} unbranched alkyl or alkenyl group, and R^1 is hydrogen, a C_1 to C_4 alkyl group or a $-CH_2-COOH$ group) or an anhydride or a salt thereof. The object of the invention of EP-A-0094814 is to overcome problems encountered with many additive concentrates containing overbased additives, namely lack of stability giving rise to sedimentation and foaming problems. The problem of EP-A-0094814 is not that of producing phenates having a TBN of greater than 300 and indeed the phenates produced by the process of the invention, although overcoming the problems of stability and foaming, have TBN values of less than 300.

[0009] Our European Application Publication No. 0095322 discloses a process for the production of either an alkaline earth metal alkyl phenate or a sulphurised alkaline earth metal alkyl phenate which process comprises reacting at elevated temperature, in the presence or absence of sulphur, an alkyl phenol with an alkaline earth metal base in the presence as solvent of either an alkylene glycol alkyl ether or a polyalkylene glycol alkyl ether of formula:

$$R(OR^1)_xOR^2$$

wherein R is a C_1 to C_6 alkyl group, R^1 is alkylene, R^2 is hydrogen or C_1 to C_6 alkyl and x is an integer in the range 1 to 6 and as catalyst an inorganic halide. It is said to be preferred to add a small amount, suitably up to 2% w/w of an acid, a suitable acid being stearic acid. The addition of stearic acid to the reactants can, it is said, enhance the ability of alkylphenates to minimise emulsion formation in water.

[0010] It can be concluded that the prior art in which carboxylic acids are employed does not address the problem of producing overbased sulphurised alkaline earth metal alkyl phenates having a TBN of greater than 300 and an acceptable viscosity.

[0011] Our copending European Application No. 0271262 claiming the same priority date as the present application provides an additive concentrate suitable for incorporation into a finished lubricating oil composition, the additive concentrate comprising:

(a) a lubricating oil,
(b) a lubricating oil soluble sulphurised or non-sulphurised alkaline earth metal hydrocarbyl phenate modified by incorporation of from greater than 2 to less than 40% by weight based on the weight of the composition of either
(i) at least one carboxylic acid having the formula:-

(I)

wherein R is a C_{10} to C_{24} alkyl or alkenyl group and R^1 is either hydrogen, a C_1 to C_4 alkyl group or a $-CH_2-COOH$ group, or an anhydride, acid chloride or ester thereof or (ii) a di-or polycarboxylic acid containing from 36 to 100 carbon atoms or an anhydride, acid chloride or ester thereof, the composition having a TBN greater than 300.

[0012] In one aspect the present invention provides a process for the production of an additive concentrate suitable for incorporation into a finished lubricating oil composition, the additive concentrate comprising:

(a) a lubricating oil,
(b) a lubricating oil soluble sulphurised alkaline earth metal hydrocarbyl phenate modified by incorporation of from greater than 10 to 35% by weight based on the weight of the concentrate of at least one carboxylic acid having the formula:-

(I)

wherein R is a C_{10} to C_{24} straight chain alkyl group and R^1 is hydrogen, or an anhydride or ester thereof or, the concentrate having a TBN greater than 300 and a viscosity at 100° of less than 1000 $mm^2.s^{-1}$ (cSt), which process comprises reacting at elevated temperature:

(A) a sulphurised alkaline earth metal hydrocarbyl phenate having a TBN less than that of the final additive concentrate,
(B) an alkaline earth metal base, either added in whole to the initial reactants, or in part to the initial reactants and the remainder in one or more portions at a subsequent stage or stages in the process,
(C) either a polyhydric alcohol having from 2 to 4 carbon atoms, a di- or tri- (C_2 to C_4) glycol, an alkylene glycol alkyl ether or a polyalkylene glycol alkyl ether,
(D) a lubricating oil,
(E) carbon dioxide added subsequent to the, or each, addition of component (B), and
(F) sufficient to provide from greater than 10 to 35% by weight based on the weight of the concentrate of at least one carboxylic acid having the formula:-

(I)

wherein R is a C_{10} to C_{24} straight chain alkyl and R^1 is hydrogen, or an anhydride or ester thereof or the weight ratios of components (A) to (F) being such as to produce a concentrate having a TBN greater than 300.

[0013] The process of the invention is advantageous because it affords a method for up-grading low TEN products of the prior art or off-specification products into high TBN products having an acceptable viscosity. Moreover, because hydrogen sulphide is not evolved during operation of the process of the invention, in contrast to processes for producing sulphurised alkaline eanh meral alkyl phenates involving the reaction of an alkyl phenol and sulphur, by the more conventional routes, the hydrogen sulphide disposal problem is avoided, thereby allowing manufacture in environmentally sansitive locations and the use of less sophisticated plant.

[0014] Component (a) of the concentrate is a lubricating oil. The lubricating oil may suitably be either an animal oil, a vegetable oil or a mineral oil. Suitably the lubricating oil may be a petroleum-derived lubricating oil, such as a naphthenic base, paraffin base or mixed base oil. Solvent neutral oils are particularly suitable. Alternatively, the lubricating oil may be a synthetic lubricating oil. Suitable synthetic lubricating oils include synthetic ester lubricating oils, which oils include diesters such as di-octyl adipate, di-octyl sebacate and tridecyladipate, or polymeric hydrocarbon lubricating oils, for example liquid polyisobutenes and poly-alpha olefins. The lubricating oil may suitably comprise from 10 to 90%, preferably from 10 to 70%, by weight of the concentrate.

[0015] Component (b) is a lubricating oil soluble sulphurised alkaline earth metal hydrocarbyl phenate modified by incorporation of from greater than 10 to 35% by weight based on the weight of the concentrate of the carboxylic acid.

[0016] Suitably the alkaline earth metal may be strontium, calcium, magnesium or barium, preferably calcium, barium

or magnesium, more preferably calcium.

[0017] The hydrocarbyl phenate moiety of the sulphurised alkaline earth metal hydrocarbyl phenate is preferably derived from at least one alkyl phenol. The alkyl groups of the alkyl phenol may be branched or unbranched. Suitable alkyl groups contain from 4 to 50, preferably from 9 to 28 carton atoms. A particularly suitable alkyl phenol is the C_{12}-alkyl phenol obtained by alkylating phenol with propylene tetramer.

[0018] The sulphurised alkaline earth metal hydrocarbyl phenate is modified by incorporation of at least one carboxylic acid having the formula (I) or an acid anhydride or ester thereof. Preferably R in the formula (I) is an unbranched alkyl group. Preferred acids of formula (I) are those wherein R is a C_{10} to C_{24}, more preferably C_{18} to C_{24} straight chain alkyl groups and R^1 is hydrogen. Examples of suitable saturated carboxylic acids of formula (I) include capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid and lignoceric acid.

[0019] 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 be obtained synthetically or may be derived from natural products, for example cotton oil, ground nut oil, coconut oil, linseed oil, palm kernel oil, olive oil, com oil, palm oil, castor oil, soyabean oil, sunflower oil, herring oil, sardine oil and tallow. Sulphurised adds and acid mixtures may also be employed. Instead of, or in addition to, the carboxylic acid there may be used the acid anhydride or the ester derivatives of the acid, preferably the acid anhydride. It is preferred however to use a carboxylic acid or mixture of carboxylic acids. A preferred carboxylic acid of formula (I) is stearic acid.

[0020] The carboxylic acid(s) having the formula (I), the acid anhydride or ester thereof is incorporated in an amount from greater than 10% to 35%, preferably from 12 to 20%, for example about 16% by weight based on the weight of the concentrate. An advantage of incorporating greater than 10% of the carboxylic acid or derivative thereof is generally relatively lower concentrate viscosity.

[0021] Suitably the alkaline earth metal may be present in the composition in an amount in the range from 10 to 20% by weight based on the weight of the concentrate.

[0022] Suitably sulphur may be present in the concentrate in an amount in the range from 1 to 6, preferably from 1.5 to 3% by weight based on the weight of the concentrate.

[0023] Suitably carbon dioxide may be present in the concentrate in an amount in the range from 5 to 20. preferably from 9 to 15% by weight based on the weight of the concentrate.

[0024] Preferably the TBN of the concentrate is greater than 350, more preferably greater than 400.

[0025] Suitably the concentrate may have a viscosity measured at 100°C of less than 1000 cSt. preferably less than 750 cSt, more preferably less than 500 cSt.

[0026] Component (A) of the reaction mixture is a sulphurised alkaline earth metal hydrocarbyl phenate having a TBN lower than that of the final product i.e. generally less than 300. Any suiphurised alkaline earth metal hydrocarbyl phenate may be employed. The sulphurised alkaline earth metal hydrocarbyl phenate may be carbonated or non-carbonated. The alkaline earth metal moiety and the hydrocarbyl phenate moiety of the sulphurised alkaline earth metal hydrocarbyl phenate may suitably be as hereinbefore described. Methods for preparing sulphurised alkaline earth metal hydrocarbyl pnenates are weil known in the art. Alternatively, the precursors of a sulphurised alkaline earth metal hydrocarbyl phenate in the form of a non-sulphurisad alkaline earth metal hydrocarbyl phenate may be employed.

[0027] The alkaline earth metal base (component B) may suitably be an alkaline earth metal oxide or hydroxide, preferably the hydroxide. Calcium hydroxide may be added for example in the form of slaked lime. Preferred alkaline earth metals are calcium, magnesium and barium and more preferred is calcium. The alkaline earth metal base must be added in an amount relative to component (A) sufficient to produce a product having a TBN in excess of 300, preferably in excess of 350. This amount will depend on a number of factors including the nature of the sulphurised alkaline earth metal hydrocarbyl phenate. Typically the weight ratio of component (B) to component (A) may suitably be in the range from 0.1 to 50, preferably from 0.2 to 5. The alkaline earth metal base (B) may be added in whole to the initial reactants, or in part to the initial reactants and the remainder in one or more portions at a subsequent stage or stages in the process. Preferably component (B) is added in a single addition to the initial reactants.

[0028] Component (C) is either a polyhydric alcohol having from 2 to 4 carbon atoms, a di-or tri-(C_2 to C_4) glycol, an alkylene glycol alkyl ether or a polyalkylene glycol alkyl ether. The polyhydric alcohol may suitably be either a dihydric alcohol, for example ethylene glycol or propylene giycol, or a trihydric alcohol, for example glycerol. The di-or tri-(C_2 to C_4) glycol may suitably be either diethylene glycol or triethylene glycol. The alkylene glycol alkyl ether or polyalkylene glycol alkyl ether may suitably be of the formula:-

$$R\,(OR^1)_xOR^2 \qquad (II)$$

wherein R is a C_1 to C_6 alkyl group, R^1 is an alkylene group, R^2 is hydrogen or C_1 to C_6 alkyl and x is an integer in the

range from 1 to 6. Suitable solvents having the formula (II) include the monomethyl or dimethyl ethers of ethylene glycol, diethylene glycol, triethylene glycol or tetraethylene glycol. A particularly suitable solvent is methyl digol ($CH_3OCH_2CH_2OCH_2CH_2OH$). Mixtures of glycols and glycol ethers of formula (II) may also be employed. Using a glycol or glycol ether of formula (II) as solvent it is preferred to use in combination therewith an inorganic halide, for example ammonium chloride, and a lower, i.e. C_1 to C_4, carboxylic acid, for example acetic acid. Preferably the component (C) is either ethylene glycol or methyl digol, the latter in combination with ammonium chloride and acetic acid.

[0029] Component (D) is a lubricating oil as hereinbefore described with reference to the concentrate composition.

[0030] Component (E) is carbon dioxide, which may be added in the form of a gas or solid, preferably in the form of a gas. In gaseous form it may suitably be blown through the reaction mixture. We have found that generally the amount of carbon dioxide incorporated increases with increasing concentrations of component (F). The carbon dioxide is preferably added subsequent to a single addition of component (B) at the conclusion of the reaction between component (A), (B), (C), (D) and (F).

[0031] Component (F) is a carboxylic acid of formula (I), or an acid anhydride or ester thereof as hereinbefore described with reference to the concentrate composition. The amount of the aforesaid required to provide from greater than 10 to 35% by weight based on the weight of the concentrate will be to a first approximation the amount defined in the concentrate. In calculating this amount allowance should be made for loss of water from carboxylic acids, for example.

[0032] The reaction may be performed in the presence of a diluent. Suitable diluents are liquids having a volatility consistent with operation of the process, i.e. having a volatility such that they are readily strippable from the reaction mixture at the conclusion of the reaction. Examples of suitable diluents include 2-ethyl hexanol, iso-octanol, iso-heptanol and tri-decanol.

[0033] Further sulphur, that is sulphur additional to that already present by way of component (A), may be added to the reaction mixture. An advantage of adding further sulphur is that it increases the amount of sulphur in the concentrate, which may be desirable for certain applications. On the other hand sulphur addition leads to the evolution of hydrogen sulphide, thereby to some extent detracting from the advantage of the invention as hereinbefore mentioned.

[0034] Preferably the reaction is carried out in the presence of a further component which is a catalyst for the reaction. As catalyst there may be used an inorganic halide which may suitably be either a hydrogen halide. an ammonium halide or a metal halide. Suitably the metal moiety of the metal halide may be inc. aluminium or an alkaline earth metal, preferably calcium. Of the halides, the chloride is preferred. Suitable catalysts include hydrogen chloride, calcium chloride, ammonium chloride, aluminium chloride and zinc chloride, preferably calcium cnloride. Suitably the amount of catalyst employed may be up to 2.0% wt/wt.

[0035] Suitably the reaction of components (A) - (F) and also the carbonation reaction may be carried out at elevated temperatures in the range from 120 to 200, preferably from about 130 to 165°C, though the actual temperature chosen for the reaction of components (A) - (F) and the carbonation may differ if desired. The pressure may be atmospheric, subatmospheric or superatmospheric.

[0036] The concentrate may be recovered by conventional means, for example by distillative stripping of component (C) and diluent (if any).

[0037] Finally, it is preferred to filter the concentrate so-obtained. Generally, the process of the invention will produce a concentrate having an acceptable viscosity, that is a viscosity of less than 1000 cSt at 100°C and can produce concentrates having a viscosity less than 750 or 500 cSt at 100°C. Moreover, the concentrates generally have desirable viscosity index properties. Such viscometric properties are advantageous because they facilitate processing (including filtration) of the concentrate. However, it is also possible to produce concentrates having a higher viscosity than 1000 cSt at 100°C, generally at higher TBN levels. Filtration of such concentrates presents a problem, which may be overcome by adding a diluent prior to to filtration and stripping the diluent off after filtration. Alternatively, or in addition, the concentrate may be diluted with lubricating oil and still retain a TBN in excess of 300, particularly if the TBN of the concentrate as produced is high, for example above 400.

[0038] In a further aspect the present invention provides an additive concentrate suitable for incorporation into a finished lubricating oil which concentrate is obtainable by reacting at elevated temperature (A) a sulphurised alkaline earth metal hydrocarbyl phenate having a TBN less than that of the final additive concentrate, (B) an alkaline earth metal base either added in whole to the initial reactants, or in part to the initial reactants and the remainder in one or more portions at a subsequent stage or stages in the process, (C) either a polyhydric alcohol having from 2 to 4 carbon atoms, a di-or tri-(C_2 to C_4) glycol, an alkylene glycol alkyl ether or a polyalkylene glycol alkyl ether, (D) a lubricating oil, (E) carbon dioxide added subsequent to the, or each, addition of component (B), and (F) sufficient to provide from greater than 10 to 35% by weight based on the weight of the concentrate of a carboxylic acid having the formula (I) or an acid anhydride or ester thereof or an acid anhydride or ester thereof, the weight ratio of components (A) to (F) being such as to produce a concentrate having a TBN greater than 300 and a viscosity at 100°C of less than 1000 $mm^2.s^{-1}$ (cSt).

[0039] A finished lubricating oil composition comprises a lubricating oil and sufficient of the additive concentrate

produced in the manner as hereinbefore described to provide a TBN in the range from 0.5 to 120.

[0040] Preferably the finished lubricating oil composition contains sufficient of the concentrate to provide a TBN in the range from 0.5 to 100.

[0041] The amount of the concentrate present in the finished lubricating oil will depend on the nature of the final use. Thus, for marine lubricating oils the amount of concentrate composition present may suitably be sufficient to provide a TBN in the range from 9 to 100 and for automobile engine lubricating oils the amount may suitably be sufficient to provide a TBN in the range from 4 to 20.

[0042] The finished lubricating oil 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 the finished lubricating oil composition either directly or through the intermediacy of the concentrate.

[0043] In addition to their use as additives for incorporation into lubricating oil compositions, the concentrates of the present invention may also find application as fuels additives.

[0044] The invention will now be further illustrated by reference to the following Examples.

[0045] In all the Examples the term "TBN" is used. The TBN is the Total Base Number in mg KOh/g as measured by the method of ASTM D2896.

[0046] In all the Examples, except otherwise expressly stated, a commercially available sulphurised calcium alkyl phenate derived from a C_{12}-alkyl phenol was employed. The phenate is supplied as a solution in lubricating oil, which forms from 36-40% w/w of the composition. The composition has a TBN of 250 and a composition as follows:- calcium (9.25% w/w), sulphur (3.25% w/w) and carbon dioxide (4.6% w/w). Where the "Charge" for any Example includes lubricating oil. this is additional to that already present in the phenate composition.

[0047] The viscosity was measured by the method of ASTM D445.

Example 1

Up-grading of Sulphurised Calcium Alkyl Phenate

[0048]

Charge	Lubricating oil	(57 g)
	Sulphurised calcium alkyl phenate	(206 g)
	Lime	(49 g)
	Stearic acid	(70 g)
	Calcium chloride	(4 g)
	2-ethyl hexanol	(112 g)

[0049] The charge was heated to 145-165° C/700 mm Hg whilst adding 36 g ethylene glycol. It was then maintained for one hour at 165° C/700 mg Hg. Carbon dioxide (50 g) was added at 165 ° C over 1 hour. The product was cooled to 125° C/700 mm Hg. Lime (33 g) was added. The temperature was raised to 165° C/700 mm Hg and held at this temperature for one hour. Carbon dioxide (25 g) was added at 165° C over one hour. The product was then stripped at 200° C/10 mm Hg. Finally the product was filtered. It was observed that the filtration rate was very fast. 437 g product and 167 g distillate were obtained.

[0050] The product was analysed for calcium, sulphur and carbon dioxide. Its TBN, BPHVI50 and Viscosity at 100° C were determined. The BPHVI50 determination is a solubility test. Results of the test are expressed on the scale 1 (highly soluble; pass), 2 (borderline) and 3 (fail).

Results	
Calcium =	13.9% w/w (corresponding to 96% retention in the product of the calcium charged.
Sulphur =	1.5% w/w (corresponding to 100% retention in the product of the sulphur charged).
Carbon Dioxide =	12.3% w/w (corresponding to 62% retention in the product of the CO_2 charged).
TBN =	395
V_{100} =	228 cSt
BPHVI50 =	1A
Stearic acid =	16% w/w

[0051] This Example demonstrates that a low TBN product can be converted to a high TBN product having an acceptable viscosity by the process of the invention.

Example 2

[0052]

Charge	Sulphurised Calcium alkyl phenate	230 g
	Lubricating oil	26 g
	Calcium chloride	3 g

Method

[0053]

(a) The charge was heated to 100° C/700 mm Hg. Stearic acid (63 g) was added and the mixture stirred for 15 minutes,
(b) 2-Ethyl hexanol (190 g) was added at 100 - 110° C/700 mm Hg,
(c) Lime (66 g) was added at 110° C/700 mm Hg,
(d) The mixture was heated to 165° C/700 mm Hg and ethylene glycol (32 g) was added quickly (one minute),

[0054] The mixture was held for 5 minutes at 165° C/700 mm Hg,

(f) Carbon dioxide (66 g) was then added at 165° C/1 bar,
(g) The solvent was recovered at 200° C/10 mm Hg, and
(h) The stripped product was filtered.

Product Weights

[0055]

Crude Product	398 g
Distillate	236 g

Product Composition After Filtration

[0056] The filtration rate was fast.

Calcium	14.1% w/w
Sulphur	2.0% w/w
CO_2	12.9% w/w
TBN	399
V_{100}	825 cSt
Stearic acid	15.8% w/w

Example 3

[0057]

Charge: As for Example 2.

Method

[0058] As for Example 2 except that the temperature was 145°C instead of 165 °C in steps (d), (e) and (f).

Product Weights

[0059]

Crude Product	402 g
Distillate	239 g

Product Composition After Filtration

[0060]

Calcium	13.9% w/w
Sulphur	1.9% w/w
CO_2	13.9% w/w
TBN	392
V_{100}	206 cSt
Stearic acid	15.7% w/w

Example 4

[0061] Charge: As for Example 2

Method

[0062] As for Example 2 except that the temperature was 130 ° C instead of 165 °C in steps (d), (e) and (f).

Products Weights

[0063]

Crude Product	377 g
Distillate	236 g

Product Composition After Filtration

[0064]

Calcium	13.7% w/w
Sulphur	2.1% w/w
CO_2	13.2% w/w
TEN	380
V_{10}	99 cSt
Stearic acid	16.7 % w/w

Example 5

[0065]

Charge: As for Example 3 except that calcium chloride was omitted.

Method

[0066] As for Example 3.

Product Weights

[0067]

Crude Product	388 g
Distillate	239 g

Product Composition After Filtration

[0068]

Calcium	11.9% w/w
Sulphur	2.1% w/w
CO_2	9.0% w/w
TBN	331
V_{100}	98 cSt
V_{40}	1490 cSt
VI	148
Stearic acid	16.2% w/w

[0069] The filtration step (h) was very difficult.

[0070] This Example, as compared with Example 3 demonstrates the desirability of using a catalyst in the process of the invention. In the absence of catalyst, although a lower V_{100} was obtained, this was achieved at the expense of reduced incorporation of calcium and carbon dioxide, and moreover filtration was difficult.

Example 6 (not according to the invention)

[0071]

Charge	Sulphurised calcium alkyl phenate	253 g
	Lubricating oil (100 SN)	26 g
	Calcium chloride	4 g
	2-Ethyl hexanol	190 g
	Stearic acid	40 g

Method

[0072]

(a) The charge was heated to 120° C/700 mm Hg and lime (36 g) was then added,
(b) The mixture was heated to 145 - 165° C whilst adding ethylene glycol (32 g),
(c) The mixture was held for one hour at 165° C/700 mm Hg,
(d) Carbon dioxide (44 g) was added at 165° C/1 bar,
(e) The mixture was cooled to 120° C and lime (25 g) was added,
(f) The mixture was held at 165° C/700 mm Hg for one hour,
(g) Carbon dioxide (22 g) was added at 165° C/1 bar,
(h) The solvent was stripped off at 200° C/10 mm Hg, and
(i) The product was filtered. The filtration rate was fast.

Product Weights

[0073]

Crude Product	401 g

(continued)

Distillate	239 g

Product Composition After Filtration

[0074]

Calcium	14.3% w/w
Sulphur	2.1% w/w
CO_2	11.3% w/w
TBN	405
V_{100}	1483 cSt
Stearic acid	10% w/w

[0075] This Example demonstrates that it is possible to produce a high TBN concentrate, though the viscosity is relatively high, by incorporating 10% w/w stearic acid.

Example 7

[0076]

Charge: As for Example 6 except that the phenate was increased from 250 g to 268 g and the stearic acid was increased from 40 g to 51 g.

Method:

[0077] As for Example 6.

Products Weights

[0078]

Crude Product	396 g
Distillate	234 g

Product Composition After Filtration

[0079]

Calcium	14.5% w/w
Sulphur	2.2% w/w
CO_2	13.1% w/w
TBN	399
V_{100}	706 cSt
Stearic acid	12.9% w/w

[0080] This Example demonstrates that a high TBN concentrate having a lower viscosity as compared with Example 6 can be produced at a stearic acid content of 12.9% w/w based on the weight of the concentrate.

Example 8

[0081]

Charge	Sulphurised calcium alkyl phenate	230 g
	Lubricating oil (SN 100)	0 g
	Calcium chloride	3 g

Method

[0082]

(a) The charge was heated to 100° C, stearic acid (99 g) was then added and the mixture was stirred for 15 minutes,
(b) 2-Ethyl hexanol (190 g) was added at 100 - 110° C,
(c) Lime (66 g) was added at 110° C/2" Hg vacuum,
(d) The mixture was heated to 145 ° C/10" Hg and ethylene glycol (32 g) was added over 20 minutes,
(e) The mixture was held for 5 minutes at 145° C/10" Hg,
(f) Carbon dioxide (66 g) was added at 145° C,
(g) The product was stripped at 200° C/30" Hg, and
(h) The product was filtered. The filtration rate was slow.

Product Weights

[0083]

Crude Product	398 g
Distillate	209 g

Product Composition After Filtration

[0084]

Calcium	11.95% w/w
Sulphur	1.65% w/w
CO_2	11.6% w/w
TBN	349
V_{100}	100 cSt
V_{40}	974 cSt
Stearic acid	24.9% w/w

[0085] This Example demonstrates that it is possible to produce a high TBN concentrate having a low viscosity at a stearic acid content of 24.9% w/w.

Comparison Test 1

[0086]

Charge: As for Example 3.

Method

[0087] As for Example 3 except that the addition of ethylene glycol in step (d) was omitted.

Product Weights

[0088]

Crude Product	382 g
Distillate	200 g

Product Composition After Filtration

[0089]

Calcium	8.4% w/w
Sulphur	2.3% w/w
CO_2	4.4% w/w
TBN	239
V_{100}	41 cSt

[0090] The filtration rate in step (h) was slow.
[0091] This is not an example according to the present invention and is included for the purpose of
[0092] demonstrating that the presence of a component (C) is essential to the performance of the process of the invention.

Example 9

[0093] Charge: As for Example 3.

Method

[0094] As for Example 3 except that the ethylene glycol addition in step (d) was reduced from 32 g to 16 g.

Product Weights

[0095]

Crude Product	399 g
Distillate	225 g

Product Composition After Filtration

[0096]

Calcium	13.7% w/w
Sulphur	2.0% w/w
CO_2	13.5% w/w
TBN	395
V_{100}	182 cSt
Stearic acid	15.8% w/w

[0097] The filtration rate in step (h) was slow.
[0098] This Example demonstrates that the addition of ethylene glycol can be reduced by 50% as compared with Example 3.

Example 10

[0099]

Charge	Sulphurised calcium alkylphenate	230 g
	Lubricating oil (100 SN)	26 g
	Ammonium chloride	4 g
	Acetic acid	2 g

Method

[0100] As for Example 3 except that in step (b) instead of 2-ethyl hexanol (190 g) there was added methyl diglycol (130 g) and in step (d) the addition of ethylene glycol was omitted.

Product Weights

[0101]

Crude Product	390 g
Distillate	166 g

Product Composition After Filtration

[0102]

Calcium	14.1% w/w
Sulphur	2.0% w/w
CO_2	14.2% w/w
TBN	398
V_{100}	210 cSt
V_{40}	3821 cSt
VI	170

[0103] The filtration rate in step (h) was rapid.
[0104] This Example demonstrates that methyl diglycol is effective as component (C).

Example 11

[0105]

Charge: As for Example 3.

Method

[0106] As for Example 3 except that in step (d) the pressure was 270 mm Hg.

Product Weight

[0107]

Crude Product	402 g
Distillate	238 g

Product Composition After Filtration

[0108]

Calcium	14.0% w/w
Sulphur	1.9% w/w
CO_2	14.4% w/w
TBN	392
V_{100}	288 cSt
Stearic acid	15.7% w/w
Stearic acid	16.2% w/w

Example 12

[0109] Charge: As for Example 3.

Method

[0110] As for Example 3 except that instead of 190 g 2-ethyl hexanol there was used 40 g.

Product Weights

[0111]

Crude Product	399 g
Distillate	90 g

Product Composition After Filtration

[0112]

Calcium	13.9% w/w
Sulphur	1.9% w/w
CO_2	12.1% w/w
TBN	408
V_{100}	387 cSt
V_{40}	7980 cSt
VI	193
Stearic acid	15.8% w/w

Example 13

[0113]

Charge	Sulphurised calcium alkyl phenate	230 g
	Stearic acid	63 g
	Calcium chloride	4 g
	C_{18} linear alpha-olefin	26 g
	2-ethyl hexanol	90 g

Method

[0114]

(a) The mixture was heated to 145 - 165° C/700 mm Hg whilst adding ethylene glycol (32 g),
(b) The mixture was held for 30 minutes at 165° C/700 mm Hg,
(c) CO_2 (38 g) was added at 165° C/1 bar,
(d) The mixture was cooled to 120° C and 2-ethyl hexanol (100 g) added,
(e) Lime (66 g) was added,
(f) The mixture was held at 165° C/700 mm Hg for 5 minutes,
(g) Carbon dioxide (66 g) was added,
(h) The solvent was recovered by stripping at 200° C/10 mm Hg,
(i) The product was filtered.

Product Weights

[0115]

Crude Product	385 g
Distillate	256 g

Product Composition After Filtration

[0116]

Calcium	14.8% w/w
Sulphur	1.9% w/w
CO_2	13.4% w/w
TBN	424
V_{100}	583 cSt
V_{40}	13,080 cSt
VI	209
Stearic acid	16.4% w/w

[0117] The filtration rate in step (i) was rapid.
[0118] This Example demonstrates that a lubricating oil can be replaced by a long carbon chain alpha-olefin (in this case C_{18}).

Example 14

[0119]

Charge	Sulphurised calcium alkyl phenate (250 TBN) derived from a mixture of $C_{12}/C_{22}/C_{24}$ alkyl phenols	233.5 g
	Lubricating oil (SN 100)	26 g
	Calcium chloride	3 g

Method

[0120]

(a) The mixture was heated to 100° C, stearic acid (63 g) was added and the mixture was stirred for 15 minutes,
(b) 2-Ethyl hexanol (194 g) was added at 100 - 110° C,
(c) Lime (66 g) was added at 110° C/2" Hg vacuum,
(d) The mixture was heated to 145° C/10" Hg and ethylene glycol (32 g) added over 20 minutes,

(e) The mixture was held for 5 minutes at 145° C/10" Hg,
(f) Carbon dioxide (66 g) was added,
(g) The product was stripped at 200° C/30" Hg,
(h) The product was filtered.

Product Weights

[0121]

Crude Product	385 g
Distillate	250 g

Product Composition After Filtration

[0122]

Calcium	14.0% w/w
Sulphur	1.84% w/w
CO_2	12.9% w/w
TBN	401
V_{100}	381 cSt
V_{40}	8385 cSt
VI	186
Stearic acid	16.4 % w/w

[0123] This Example demonstrates that sulphurised calcium alkyl phenates derived from a mixture of $C_{12}/C_{22}/C_{24}$ alkyl phenols can be upgraded.

Example 15

[0124]

Charge	Sulphurised calcium alkyl phenate	181 g
	Lubricating oil (SN 100)	50 g
	Calcium chloride	4 g
	Rape Top Fatty Acid	62 g
	2-Ethyl hexanol	190 g

Method

[0125]

(a) The mixture was heated to 120° C,
(b) Lime (43 g) was added at 120° C/2" Hg vacuum,
(c) Ethylene glycol (32 g) was added at 145 - 165° C/2" Hg,
(d) The mixture was held at 165° C/2" Hg for 1 hour,
(e) Carbon dioxide (44 g) was added,
(f) The mixture was cooled to 130° C and lime (29 g) was added at 130 °C/2" Hg,
(g) The mixture was held at 165° C/2" Hg for 1 hour,
(h) Lime (22 g) was added at 165° C,
(i) The product was stripped at 200° C/30" Hg,
(j) The product was filtered.

Product Weights

[0126]

Crude Product	382 g
Distillate	230 g

Product Composition After Filtration

[0127]

Calcium	14.0% w/w
Sulphur	1.8% w/w
CO_2	12.3% w/w
TBN	374
V_{100}	176 cSt
V_{40}	2826 cSt
VI	172
Carboxylic acid content	16.2 % w/w

[0128] This Example demonstrates that Rape Top Fatty Acid can be used in the process of the invention.

Example 16

[0129]

Charge	Sulphurised calcium alkyl phenate	230 g
	Lubricating oil (SN 100)	26 g
	Calcium chloride	3 g

Method

[0130] As for Example 2 except that in step (a) instead of stearic acid (63 g) there was used Tall Oil Fatty Acid (63 g).

Product Weights

[0131]

Crude Product	380 g
Distillate	223 g

Product Composition After Filtration

[0132]

Calcium	14.0% w/w
Sulphur	2.09% w/w
CO_2	9.7% w/w
TBN	380
V_{100}	263 cSt
Carboxylic acid content	16.6 % w/w based on the weight of product.

[0133] This Example demonstrates that Tall Oil Fatty Acid can be used in the process of the invention.

Example 17

[0134]

Charge: As for Example 16.

Method

[0135] As for Example 16 except that instead of Tall Oil Fatty Acid (63 g) there was used a mixture of 52 g polyisobutene succinic anhydride (PIBSA) in SN 100 lubricating oil (TBN = 60 mg KOH/g) and stearic acid (47 g).

Product Weights

[0136]

Crude Product	390 g
Distillate	219 g

Product Composition After Filtration

[0137]

Calcium	13.1% w/w
Sulphur	1.8% w/w
CO_2	12.5% w/w
TBN	360
V_{100}	416 cSt
V_{40}	12,690 cSt
VI	164
Carboxylic acid content	12.1 % w/w) based on the
Anhydride content	7.2 % w/w) weight of product

[0138] This Example demonstrates that the carboxylic acid can be replaced in part by PIBSA in the process of the invention.

Example 18

[0139]

Charge: As for Example 16.

Method

[0140] As for Example 16 except that instead of Tall Oil Fatty Acid (63 g) there was used behenic acid (63 g).

Product Weights

[0141]

Crude Product	402 g
Distillate	247 g

Product Composition After Filtration

[0142]

Calcium	12.4% w/w
Sulphur	1.9% w/w
CO_2	11.4% w/w
TBN	354
V_{100}	141 cSt
Behenic acid	15.7 % w/w

[0143] This Example demonstrates that behenic acid can be used as the carboxylic acid in the process of the invention.

Example 19

[0144]

Charge: As for Example 15 except that instead of Rape Top Fatty Acid (62 g) there was used palmitic acid (56.2 g).

Method

[0145] As for Example 15 except that steps (f), (g) and (h) were omitted.

Product Weights

[0146]

Crude Product	312 g
Distillate	222 g

Product Composition After Filtration

[0147]

Calcium	11.7% w/w
Sulphur	1.9% w/w
CO_2	8.2% w/w
TBN	332
V_{100}	70 cSt
V_{40}	831 cSt
VI	156
Palmitic acid	18.0 % w/w

[0148] This Example demonstrates that palmitic acid can be used in the process of the invention.

Example 20

[0149]

Charge: As for Example 15.

Method

[0150] As for Example 15 except that steps (f), (g) and (h) were omitted.

Product Weights

[0151]

Crude Product	334 g
Distillate	234 g

Product Composition After Filtration

[0152]

Calcium	11.8% w/w
Sulphur	1.8% w/w
CO_2	10.9% w/w
TBN	321
V_{100}	168 cSt
V_{40}	1009 cSt
VI	286
Palmitic acid	18.6 % w/w based on the weight of product.

Comparison Test 2

[0153]

Charge	Sulphurised calcium alkyl phenate	230 g
	Lubricating oil	26 g
	Calcium chloride	3 g

Method

[0154]

(a) The mixture was heated to 100° C and 2-ethyl hexanol (190 g) was added,
(b) Acetic acid (14 g) was added,
(c) The mixture became thick and heterogeneous and assumed a green colouration. Stirring was ineffective. The reaction was discontinued.

[0155] This Test is not an example according to the present invention and is included only for the purpose of demonstrating that lower carboxylic acids, in this case acetic acid, can not be used in the process of the invention.

Example 21

[0156]

Charge: As for Example 16 except that instead of the commercially available sulphurised calcium alkyl phenate there was used an uncarbonated commercially available sulphurised calcium C_{12}-alkyl phenate (145 TBN).

Method

[0157] As for Example 16 except that in step (c) the amount of lime was increased from 66 g to 83 g and in step (f) the amount of carbon dioxide was increased from 66 g to 83 g.

Product Weights

[0158]

Crude Product	421 g
Distillate	246 g

Product Composition After Filtration

[0159]

Calcium	13.7% w/w
Sulphur	1.9% w/w
CO_2	10.3% w/w
TBN	383
V_{100}	137 cSt
V_{40}	2119 cSt
VI	163
Carboxylic acid	15.0% w/w

[0160] This Example demonstrates that an uncarbonated sulphurised calcium alkyl phenate of low initial TBN can be used in the process of the invention.

Example 22

[0161]

Charge:	A carbonated sulphurised calcium alkyl phenate (150 TBN)	253 g
	Stearic acid	40 g
	2-Ethyl hexanol	90 g
	Calcium chloride	4 g

Method

[0162]

(a) The mixture was heated from 145 to 165° C/700 mm Hg whilst adding ethylene glycol (32 g),
(b) The mixture was held at 165° C/700 mm Hg for 30 minutes,
(c) Carbon dioxide (38 g) was added at 165° C/1 bar,
(d) The mixture was cooled to 120° C and there was added 2-ethyl hexanol (100 g) and lime (76 g),
(e) The mixture was held for 60 minutes at 165° C/700 mm Hg,
(f) Carbon dioxide (82 g) was added at 165° C/1 bar,
(g) Solvent was recovered at 200° C/10 mm Hg, and
(h) The product was filtered.

Product Weights

[0163]

Product Weight	390 g

Product Composition After Filtration

[0164]

Calcium	14.4% w/w
Sulphur	2.3% w/w
CO_2	11.6% w/w
TBN	402
V_{100}	674 cSt
Stearic acid	10.3% w/w

[0165] This Example demonstrates that a low (150) TBN sulphurised calcium alkyl phenate can be upgraded to a high TBN product.

Example 23

[0166]

Charge: As for Example 14 except that instead of the sulphurised calcium alkyl phenate derived from a mixture of alkyl phenols there was used the commercially available sulphurised calcium alkyl phenate derived from a C_{12}-alkyl phenol (250 TBN).

Method

[0167] As for Example 14 except that in step (b) instead of 2-ethyl hexanol (194 g) there was used iso-heptanol (190 g) and in step (d) the ethylene glycol was added quickly (within 1 minute).

Product Weights

[0168]

Crude Product	402 g
Distillate	239 g

Product Composition After Filtration

[0169]

Calcium	13.9% w/w
Sulphur	1.9% w/w
CO_2	12.0% w/w
TBN	391
V_{100}	313 cSt
V_{40}	6700 cSt
VI	177
Stearic acid	15.7% w/w

[0170] The filtration rate was rapid.

[0171] This Example demonstrates that iso-heptanol may be used as solvent in the process of the invention.

Claims

1. A process for the production of an additive concentrate suitable for incorporation into a finished lubricating oil composition, the additive concentrate comprising:

(a) a lubricating oil,
(b) a lubricating oil soluble sulphurised alkaline earth metal hydrocarbyl phenate modified by incorporation of from greater than 10 to 35% by weight based on the weight of the concentrate of at least one carboxylic acid having the formula:-

(I)

wherein R is a C_{10} to C_{24} straight chain alkyl group and R^1 is hydrogen, or an anhydride or ester thereof the concentrate having a TBN greater than 300 and a viscosity at 100° C of less than 1000 $mm^2.s^{-1}$ (cSt), which process comprises reacting at elevated temperature:
(A) a sulphurised alkaline earth metal hydrocarbyl phenate having a TBN less than that of the final additive concentrate,
(B) an alkaline earth metal base, either added in whole to the initial reactants, or in part to the initial reactants and the remainder in one or more portions at a subsequent stage or stages in the process,
(C) either a polyhydric alcohol having from 2 to 4 carbon atoms, a di- or tri- (C_2 to C_4) glycol, an alkylene glycol alkyl ether or a polyalkylene glycol alkyl ether,
(D) a lubricating oil,
(E) carbon dioxide added subsequent to the, or each, addition of component (B), and
(F) sufficient to provide from greater than 10 to 35% by weight based on the weight of the concentrate of at least one carboxylic acid having the formula:-

(I)

wherein R is a C_{10} to C_{24} straight chain alkyl and R^1 is hydrogen, or an anhydride or ester thereof, the weight ratios of components (A) to (F) being such as to produce a concentrate having a TBN greater than 300.

2. A process according to claim 1 wherein the lubricating oil comprises from 10 to 90% by weight of the concentrate.

3. A process according to either claim 1 or claim 2 wherein the alkaline earth metal of the lubricating oil soluble sulphurised alkaline earth metal hydrocarbyl phenate is calcium, magnesium or barium.

4. A process according to claim 3 wherein the alkaline earth metal is calcium.

5. A process according to any one of the preceding claims wherein the hydrocarbyl phenate moiety of the oil soluble sulphurised alkaline earth metal hydrocarbyl phenate is derived from at least one alkyl phenol, the alkyl group or groups of the alkyl phenol or phenols containing from 9 to 28, carbon atoms.

6. A process according to claim 5 wherein the hydrocarbyl phenate moiety is derived from a C_{12}-alkyl phenol obtained by alkylating phenol with propylene tetramer.

7. A process according to any one of claims 1 to 6 wherein there is incorporated a mixture of carboxylic acids of formula (I), which mixture is a commercial grade containing a range of acids, including both saturated and unsaturated acids.

8. A process according to any one of claims 1 to 6 wherein there is incorporated stearic acid.

9. A process according to any one of the preceding claims wherein the carboxylic acid, anhydride or ester thereof is incorporated into component (b) in an amount in the range from 12 to 20% by weight based on the weight of the concentrate.

10. A process according to any one of the preceding claims wherein the TBN of the concentrate is greater than 350.

11. A process according to claim 10 wherein the TBN of the concentrate is greater than 400.

12. A process according to any one of the preceding claims wherein the viscosity of the concentrate at 100° C is less than 750 cSt.

13. A process according to claim 12 wherein the viscosity of the concentrate at 100° C is less than 500 $mm^2.s^{-1}$ (cSt).

14. A process according to any one of the preceding claims wherein component (B) is lime.

15. A process according to any one of the preceding claims wherein the weight ratio of component (B) to component (A) is in the range from 0.2 to 5.

16. A process according to any one of the preceding claims wherein component (C) is ethylene glycol.

17. A process according to any one of claims 1 to 15 wherein component (C) is methyl digol.

18. A process according to any one of the preceding claims wherein the carbon dioxide (component E) is added subsequent to a single addition of component (B) at the conclusion of the reaction between components (A) to (D) and (F).

19. A process according to any one of the preceding claims wherein a diluent is present.

20. A process according to any one of the preceding claims wherein sulphur additional to that already present by way of component (A) is added to the reaction mixture.

21. A process according to any one of the preceding claims wherein the reaction is carried out in the presence of a catalyst.

22. A process according to claim 21 wherein the catalyst is an inorganic halide.

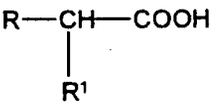
23. A process according to claim 22 wherein the catalyst is calcium chloride.

24. An additive concentrate suitable for incorporation into a finished lubricating oil which concentrate is obtainable by reacting at elevated temperature (A) a sulphurised alkaline earth metal hydrocarbyl phenate having a TBN less than that of the final additive concentrate, (B) an alkaline earth metal base either added in whole to the initial reactants, or in part to the initial reactants and the remainder in one or more portions at a subsequent stage or stages in the process, (C) either a polyhydric alcohol having from 2 to 4 carbon atoms, a di-or tri-(C_2 to C_4) glycol, an alkylene glycol alkyl ether or a polyalkylene glycol alkyl ether, (D) a lubricating oil, (E) carbon dioxide added subsequent to the, or each, addition of component (B), and (F) sufficient to provide from greater than 10 to 35% by weight based on the weight of the concentrate of a carboxylic acid having the formula (I) or an acid anhydride or ester thereof or the weight ratio of components (A) to (F) being such as to produce a concentrate having a TBN greater than 300 and a viscosity at 100° C of less than 1000 $mm^2.s^{-1}$ (cSt).

Patentansprüche

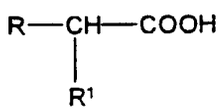
1. Verfahren zur Herstellung eines Additivkonzentrats, geeignet zum Einbringen in eine fertige Schmierölzusammensetzung, wobei das Additivkonzentrat umfaßt:

(a) ein Schmieröl,
(b) ein schmieröllösliches, sulfuriertes Erdalkalimetallhydrocarbylphenat, welches modifiziert ist durch Einbringen von mehr als 10 bis 35 Gew.-%, bezogen auf das Gewicht des Konzentrats, von mindestens einer Carbonsäure mit der Formel:



worin R einen geradkettigen (C_{10}-C_{24})Alkylrest darstellt und R^1 Wasserstoff ist, oder eines Anhydrids oder Esters davon, wobei das Konzentrat eine TBN von mehr als 300 und eine Viskosität bei 100°C von weniger als 1000 $mm^2.s^{-1}$ (cSt) besitzt, welches Verfahren das Umsetzen bei erhöhter Temperatur von:

(A) einem sulfurierten Erdalkalihydrocarbylphenat mit einer geringeren TBN als das fertige Additivkonzentrat,
(B) einer Erdalkalimetallbase, welche entweder zur Gänze den ursprünglichen Reaktanten zugesetzt wird oder in einem Teil zu den ursprünglichen Reaktanten zugesetzt wird und der Rest in einem oder mehreren Teilen in einer darauffolgenden Stufe oder in darauffolgenden Stufen in der Reaktion zugesetzt wird,
(C) entweder einem mehrwertigen Alkohol mit 2 bis 4 Kohlenstoffatomen, einem Di- oder Tri(C_2-C_4)glykol, einem Alkylenglykolalkylether oder einem Polyalkylenglykolalkylether,
(D) einem Schmieröl,
(E) Kohlendioxid, welches nachfolgend zur Zugabe oder zu jeder Zugabe der Komponente (B) hinzugefügt wird und
(F) in einer ausreichenden Menge, um von mehr als 10 bis 35 Gew.-%, bezogen auf das Gewicht des Konzentrats zur Verfügung zu stellen, von mindestens einer Carbonsäure mit der Formel:



worin R einen geradkettigen (C_{10}-C_{24})Alkylrest darstellt und R^1 Wasserstoff ist, oder eines Anhydrids oder Esters davon,

wobei die Gewichtsverhältnisse der Komponenten (A) bis (F) derart sind, daß ein Konzentrat mit einer TBN von mehr als 300 hergestellt wird.

2. Verfahren nach Anspruch 1, worin das Schmieröl 10 bis 90 Gew.-% des Konzentrats ausmacht.

3. Verfahren nach Anspruch 1 oder 2, worin das Erdalkalimetall des schmieröllöslichen, sulfurierten Erdalkalimetallhydrocarbylphenats Calcium, Magnesium oder Barium ist.

4. Verfahren nach Anspruch 3, worin das Erdalkalimetall Calcium ist.

5. Verfahren nach einem der vorstehenden Ansprüche, worin sich der Hydrocarbylphenatrest des öllöslichen sulfurierten Erdalkalimetallhydrocarbylphenats von mindestens einem Alkylphenol herleitet, wobei die Alkylgruppe oder die Alkylgruppen des Alkylphenols oder der Alkylphenole 9 bis 28 Kohlenstoffatome enthält bzw. enthalten.

6. Verfahren nach Anspruch 5, worin sich der Hydrocarbylphenatrest aus einem C_{12}-Alkylphenol herleitet, welches durch Alkylieren von Phenol mit einem Propylentetramer erhalten wird.

7. Verfahren nach einem der Ansprüche 1 bis 6, worin ein Gemisch aus Carbonsäuren der Formel (I) eingebracht ist, welches Gemisch eine handelsübliche Qualität ist, welche einen Bereich vor Säuren, einschließlich sowohl gesättigter als auch ungesättigter Säuren, enthält.

8. Verfahren nach einem der Ansprüche 1 bis 6, worin Stearinsäure eingebracht ist.

9. Verfahren nach einem der vorstehenden Ansprüche, worin die Carbonsäure, das Anhydrid oder der Ester davon in einer Menge im Bereich von 12 bis 20 Gew.-%, bezogen auf das Gewicht des Konzentrats in Komponente (b) eingebracht ist.

10. Verfahren nach einem der vorstehenden Ansprüche, worin die TBN des Konzentrats mehr als 350 beträgt.

11. Verfahren nach Anspruch 10, worin die TBN des Konzentrats mehr als 400 beträgt.

12. Verfahren nach einem der vorstehenden Ansprüche, worin die Viskosität des Konzentrats bei 100°C weniger als 750 cSt beträgt.

13. Verfahren nach Anspruch 12, worin die Viskosität des Konzentrats bei 100°C weniger als 500 $mm^2.s^{-1}$ (cSt) beträgt.

14. Verfahren nach einem der vorstehenden Ansprüche, worin die Komponente (B) Kalk ist.

15. Verfahren nach einem der vorstehenden Ansprüche, worin das Gewichtsverhältnis von Komponente (B) zu Komponente (A) im Bereich von 0,2 bis 5 beträgt.

16. Verfahren nach einem der vorstehenden Ansprüche, worin die Komponente (C) Ethylenglykol ist.

17. Verfahren nach einem der Ansprüche 1 bis 15, worin die Komponente (C) Methyl-Digol ist.

18. Verfahren nach einem der vorstehenden Ansprüche, worin das Kohlendioxid (Komponente E) nach einer einzelnen Zugabe der Komponente (B) am Ende der Reaktion zwischen den Komponenten (A) bis (D) und (F) zugesetzt wird.

19. Verfahren nach einem der vorstehenden Ansprüche, worin ein Verdünnungsmittel vorhanden ist.

20. Verfahren nach einem der vorstehenden Ansprüche, worin Schwefel zusätzlich zu dem bereits auf Grund der Komponente (A) vorliegenden Schwefel zum Reaktionsgemisch zugefügt wird.

21. Verfahren nach einem der vorstehenden Ansprüche, worin die Reaktion in Gegenwart eines Katalysators ausgeführt wird.

22. Verfahren nach Anspruch 21, worin der Katalysator ein anorganisches Halogenid ist.

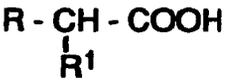
23. Verfahren nach Anspruch 22, worin der Katalysator Calciumchlorid ist.

24. Additivkonzentrat, geeignet zum Einbringen in ein fertiges Schmieröl, wobei das Konzentrat erhältlich ist durch Umsetzen bei erhöhter Temperatur von (A) einem sulfurierten Erdalkalimetallhydrocarbylphenat mit einer geringeren TBN als das fertige Additivkonzentrat, (B) einer Erdalkalimetallbase, welche entweder zur Gänze den ursprünglichen Reaktanten zugesetzt wird oder in einem Teil zu den ursprünglichen Reaktanten zugesetzt wird und der Rest in einem oder mehreren Teilen in einer darauffolgenden Stufe oder in darauffolgenden Stufen in der Reaktion zugesetzt wird, (C) entweder einem mehrwertigen Alkohol mit 2 bis 4 Kohlenstoffatomen, einem Di- oder Tri(C_2-C_4)glykol, einem Alkylenglykolalkylether oder einem Polyalkylenglykolalkylether, (D) einem Schmieröl, (E) Kohlendioxid, welches nachfolgend zur Zugabe oder zu jeder Zugabe der Komponente (B) hinzugefügt wird und (F) in einer ausreichenden Menge, um von mehr als 10 bis 35 Gew.-%, bezogen auf das Gewicht des Konzentrats zur Verfügung zu stellen, von einer Carbonsäure mit der Formel (I) oder eines Säureanhydrides oder Esters davon, wobei das Gewichtsverhältnis der Komponenten (A) bis (F) derart ist, daß ein Konzentrat mit einer TBN von mehr als 300 und einer Viskosität bei 100°C von weniger als 1000 $mm^2.s^{-1}$ (cSt) erzeugt wird.

Revendications

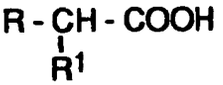
1. Procédé de production d'un concentré d'additif convenant pour être incorporé dans une composition d'huile lubrifiante formant un produit fini, ce concentré d'additif comprenant :

(a) une huile lubrifiante,
(b) un phénate de métal alcalino-terreux, hydrocarboné et sulfuré, soluble dans l'huile lubrifiante, qui a été modifié par incorporation d'une proportion, allant d'une valeur supérieure à 10 à 35 % en poids, rapporté au poids du concentré, d'au moins un acide carboxylique de formule :



dans laquelle R est un radical alcoyle à chaîne droite en C_{10} à C_{24} et R^1 est l'hydrogène, ou d'un anhydride ou un ester d'un tel acide, ce concentré ayant un IAT supérieur à 300 et une viscosité à 100°C inférieure à 1000 $mm^2.s^{-1}$ (cSt), ce procédé consistant à faire réagir, à température élevée :

(A) un phénate de métal alcalino-terreux, hydrocarboné et sulfuré, ayant un IAT inférieur à celui du concentré d'additif final,
(B) une base de métal alcalino-terreux ajoutée soit en totalité aux produits réagissants initiaux, soit en partie à ces produits réagissants initiaux et le reste en une ou plusieurs portions à un stade ou des stades ultérieurs au cours du procédé,
(C) un alcool polyhydrique ayant de 2 à 4 atomes de carbone, un diglycol ou triglycol en C_2 à C_4, un alcoyléther d'alcoyléneglycol ou un alcoyléther de polyalcoyléneglycol,
(D) une huile lubrifiante,
(E) du bioxyde de carbone ajouté à la suite de l'addition, ou de chaque addition, de composant (B) et
(F) suffisamment, pour donner une proportion allant d'une valeur supérieure à 10 à 35 % en poids, rapporté au poids de concentré, d'au moins un acide carboxylique de formule :



dans laquelle R est un radical alcoyle à chaîne droite en C_{10} à C_{24} et R^1 est l'hydrogène, ou d'un anhydride ou un ester d'un tel acide,

les rapports en poids des composants (A) à (F) étant tels qu'ils produisent un concentré ayant un IAT supérieur à 300.

2. Procédé suivant la revendication 1, selon lequel l'huile lubrifiante comprend de 10 à 90 % en poids du concentré.

3. Procédé suivant l'une des revendications 1 ou 2, selon lequel le métal alcalino-terreux du phénate de métal alcalino-terreux, hydrocarboné et sulfuré, soluble dans l'huile lubrifiante est le calcium, le magnésium ou le baryum.

4. Procédé suivant la revendication 3, selon lequel le métal alcalino-terreux est le calcium.

5. Procédé suivant l'une quelconque des revendications précédentes, selon lequel la partie phénate hydrocarboné du phénate de métal alcalino-terreux, hydrocarboné et sulfuré, soluble dans l'huile provient d'au moins un alcoylphénol, le ou les radicaux alcoyle du ou des alcoyphénols contenant de 9 à 28 atomes de carbone.

6. Procédé suivant la revendication 5, selon lequel la partie phénate hydrocarboné provient d'un alcoylphénol en C_{12} obtenu en alcoylant un phénol au moyen d'un tétramère de propylène.

7. Procédé suivant l'une quelconque des revendications 1 à 6, selon lequel il est incorporé un mélange d'acides carboxyliques de formule (I), lequel mélange est d'une qualité commerciale contenant une variété d'acides, parmi lesquels à la fois des acides saturés et des acides insaturés.

8. Procédé suivant l'une quelconque des revendications 1 à 6, selon lequel il est incorporé de l'acide stéarique.

9. Procédé suivant l'une quelconque des revendications précédentes, selon lequel l'acide carboxylique, l'anhydride ou l'ester de cet acide est incorporé dans le composant (b) dans une proportion comprise entre 12 et 20 % en poids, rapporté au poids du concentré.

10. Procédé suivant l'une quelconque des revendications précédentes, selon lequel l'IAT du concentré est supérieur à 350.

11. Procédé suivant la revendication 10, selon lequel l'IAT du concentré est supérieur à 400.

12. Procédé suivant l'une quelconque des revendications précédentes, selon lequel la viscosité du concentré à 100 °C est inférieure à 750 cSt.

13. Procédé suivant la revendication 12, selon lequel la viscosité du concentré à 100 °C est inférieure à 500 $mm^2.s^{-1}$ (cSt).

14. Procédé suivant l'une quelconque des revendications précédentes, selon lequel le composant (B) est la chaux.

15. Procédé suivant l'une quelconque des revendications précédentes, selon lequel le rapport en poids du composant (B) au composant (A) est compris entre 0,2 et 5.

16. Procédé suivant l'une quelconque des revendications précédentes, selon lequel le composant (C) est l'éthylèneglycol.

17. Procédé suivant l'une quelconque des revendications 1 à 15, selon lequel le composant (C) est le méthyldigol.

18. Procédé suivant l'une quelconque des revendications précédentes, selon lequel l'anhydride carbonique (composant E) est ajouté à la suite d'une addition unique de composant (B) lors de l'achèvement de la réaction entre les composants (A) à (D) et (F).

19. Procédé suivant l'une quelconque des revendications précédentes, selon lequel un diluant est présent.

20. Procédé suivant l'une quelconque des revendications précédentes, selon lequel on ajoute au mélange de réaction du soufre en supplément par rapport à celui déjà présent au moyen du composant (A).

21. Procédé suivant l'une quelconque des revendications précédentes, selon lequel la réaction est conduite en présence d'un catalyseur.

22. Procédé suivant la revendication 21, selon lequel le catalyseur est un halogénure non organique.

23. Procédé suivant la revendication 22, selon lequel le catalyseur est le chlorure de calcium.

24. Concentré d'additif convenant pour être incorporé dans une huile de lubrification constituant un produit fini, lequel concentré peut être obtenu en faisant réagir à température élevée (A) un phénate de métal alcalino-terreux, hydrocarboné et sulfuré, ayant un IAT inférieur à celui du concentré d'additif final, (B) une base de métal alcalino-terreux ajoutée soit en totalité aux produits réagissants initiaux, soit en partie à ces produits réagissants initiaux et le reste en une ou plusieurs portions à un stade ou des stades ultérieurs au cours du procédé, (C) un alcool polyhydrique ayant de 2 à 4 atomes de carbone, un diglycol ou triglycol en C_2 à C_4, un alcoyléther d'alcoylèneglycol ou un alcoyléther de polyalcoylèneglycol, (D) une huile lubrifiante, (E) de l'anhydride carbonique ajouté à la suite de l'addition, ou de chaque addition, de composant (B) et (F) suffisamment pour donner une proportion allant d'une valeur supérieure à 10 à 35 % en poids, rapporté au poids de concentré, d'un acide carboxylique de formule (I) ou d'un anhydride ou un ester d'un tel acide, les rapports en poids des composants (A) et (F) étant tels qu'ils produisent un concentré ayant un IAT supérieur à 300 et une viscosité à 100°C inférieure à 1000 $mm^2.s^{-1}$ (cSt).