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(54) Process for the preparation of sulphurized salicylates.

(57) Process for the preparation of a sulphurized, metal aliphatic hydrocarbon-substituted salicylate, wherein an aliphatic hydrocarbon-substituted phenol is sulphurized, and the resulting product is transformed into an alkali metal salicylate with an alkali metal hydroxide and carbon dioxide.

The product thus obtained is optionally transformed in an overbased metal salicylate.

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PROCESS FOR THE PREPARATION OF SULPHURIZED SALICYLATES

This invention relates to a process for the preparation of sulphurized, optionally overbased metal aliphatic hydrocarbon-substituted salicylates, to products thus prepared and to oil compositions containing them.

From British patent specification 1,287,812 such products and oil compositions containing them as detergents and wear inhibitors are already known. It discloses the reaction of an aliphatic hydrocarbon-substituted salicylic acid, or a metal salt thereof, with elemental sulphur, an alkaline earth base, e.g. a hydroxide, and a solvent, such as ethylene glycol, at at least 150 °C, and optionally further reaction with carbon dioxide. A similar process is disclosed in British patent specification 1,194,503.

However, it has been found that this known process shows the disadvantage of a substantial degree of decarboxylation during the reaction of the salicylic acid, or a metal salt thereof, with sulphur.

It has now been found that this problem can be avoided by first sulphurizing an aliphatic hydrocarbon-substituted phenol and then transforming the reaction product into a salicylic acid or metal salt thereof.

This invention therefore relates to a process for the preparation of sulphurized metal aliphatic hydrocarbon-substituted salicylates, characterized in that an aliphatic hydrocarbon-substituted phenol is sulphurized and the resulting product is transformed into an alkali metal salicylate with an alkali metal hydroxide and carbon dioxide. The product thus obtained is optionally transformed into an overbased metal salicylate.

The invention furthermore relates to the products thus prepared and to oil compositions containing them.

Suitable aliphatic hydrocarbon-substituted phenols are described in the above-mentioned British patent specifications. Preferred are C_{8-30}-alkyl phenols.

These phenols may be sulphurized with sulphur halides, preferably sulphur chlorides such as SCl_2 and in particular S_2Cl_2. Elemental sulphur can also be used.

The sulphurization with sulphur halide is preferably carried out in a solvent such as aliphatic hydrocarbons, e.g. n-hexane. The use of aromatic solvents, such as xylene, should be avoided otherwise these solvents may also be sulphurized with the sulphur halide.

The reaction can be carried out at ambient temperature, although some heating may be applied, e.g. up to 60 °C.

The sulphurization with elemental sulphur can be carried out by contacting the phenols with sulphur in the presence of a solvent such as ethylene glycol and a base catalyst such as lime ($Ca(OH)_2$) at a temperature in the range of 100-250 °C, preferably 150-225 °C, whereby the final temperature should preferably be at least 175 °C and more preferably at least 195 °C.

The above-mentioned solvent used in the sulphurization step preferably is an alkylene or polyalkylene glycol or a lower alkyl monoether thereof, as disclosed in the above-mentioned British patent specifications 1,287,812 and 1,194,503. Most preferably the solvent is ethylene glycol.

A promotor such as carboxylic acid or a metal salt thereof, as described in British patent specification 1,194,503, may also be present in the sulphurization step.

The molar ratio of S:substituted phenol is e.g. 0.25 to 3, preferably 0.5 to 2.

The resulting product is acidified if necessary to transform any phenate to phenol.

The transformation of the sulphurized phenols into a salicylate is preferably carried out via the Kolbe synthesis by reaction with sodium hydroxide and carbon dioxide as described in the above-mentioned British patent specifications and in British patent specification 786,167.

This sulphurized salicylic acid salt is a useful intermediate for the preparation of the corresponding overbased salicylates, which combine good detergency with reduced wear in lubricating oil compositions. Suitable metals of the overbased metal salicylate are e.g. alkali metals, such as Li, Cs, Na and K, alkaline earth metals, such as Ca, Ba, Sr and Mg, and polyvalent metals, such as Zn and Cr.

Alkaline earth metals, such as calcium, barium and magnesium are preferred. Therefore the sulphurized alkali metal salicylate is suitably transformed into the corresponding salicylic acid, which is converted with a basic alkaline earth metal compound, preferably the hydroxide, and carbon dioxide into an overbased alkaline earth metal salicylate. The degree of overbasing is expressed as the basicity index (BI) defined as the equivalent ratio of metal: salicylic acid.

The overbasing of the sulphurized alkali metal salicylate may be carried out by acidification and reaction in a solvent, such as a hydrocarbon solvent, preferably an aromatic hydrocarbon solvent, such as xylene, with the basic metal compound and carbon dioxide, as described in e.g. British patent specification 786,167.

To the resulting reaction mixture a light mineral oil may be added and then the hydrocarbon solvent, and any water formed may be removed by distillation.

The resulting oil solution of the sulphurized product may be filtered, if desired, and then be added to an oil, such as a lubricating oil or a fuel oil, including gasoline.

Before or after sulphurization the product may be reacted with a boron compound, such as boric acid, as described in the copending British patent application 8330441.

The reaction products of this invention including mixtures thereof can be incorporated in oil compositions, in particular lubricating oil compositions or concentrates or fuels, e.g., automotive crankcase oils, in concentrations within the range of 0.001 to 65, in particular 0.1 to 15 %w based on the weight of the total compositions.

The lubricating oils to which the additives of the invention can be added include not only mineral lubricating oils, but synthetic oils also. Synthetic hydrocarbon-lubricating oils may also be employed, as well as non-hydrocarbon synthetic oils including dibasic acid esters such as di-2-ethyl hexyl sebacate, carbonate esters, phosphate esters, halogenated hydrocarbons, polysilicones, polyglycols, glycol esters such as C_{13} oxo acid diesters of tetraethylene glycol, etc. Mixtures of these oils, in particular of mineral lubricating oils, including hydrogenated oils, and synthetic lubricating oils, can also be used.

When used in gasoline or fuel oil, e.g., diesel fuel, etc., then usually 0.001 to 0.5 %w, based on the weight of the total composition of the reaction product will be used. Usually concentrates comprising e.g. 15 to 65 %w of said reaction product in a hydrocarbon diluent and 85 to 35 %w mineral lubricating oil, are prepared for ease of handling.

In the above compositions other additives may also be present, including dyes, pour point depressants, anti-wear, e.g., tricresyl phosphate, zinc dithiophosphates, antioxidants such as phenyl-alpha-naphthyl-amine, bis-phenols such as 4,4'-methylene bis (3,6-di-tert-butylphenol), viscosity index improvers, such as hydrogenated (co)polymers of conjugated dienes and optionally styrene, ethylene-higher olefin copolymers, polymethylacrylates, polyisobutylene, and the like as well as ashless dispersants, such as reaction products of polyisobutylene, maleic anhydride and amines and/or polyols, or other metal-containing detergents, such as overbased metal salicylates.

Reaction products of amines, formaldehyde and alkyl phenols (Mannich bases) can also be present.

The invention is further illustrated by the following Examples.

Example 1

Preparation of sulphurized alkyl phenol.

A reaction vessel (5 litre) was charged with 2000 g tetrapropenylphenol (7520 meq), 122 g calcium hydroxide (3300 meq), 364 g elemental sulphur (11375 meq) and 74 g ethylene glycol. Under stirring this mixture was heated to 125 °C and kept at that temperature for one hour. The temperature was then raised to 150 °C and kept at that temperature for one hour at a pressure of about 550 mm Hg. Then the temperature was raised to 195 °C and kept at 50-60 mm Hg for two hours. The reaction product was cooled, solvent was added and the mixture was filtered. The solvent was removed leaving a dark, viscous product (yield: 2266 g; S: 8.2 %w) (Product A).

Example 2

Preparation of sulphurized alkyl phenol.

To a reaction vessel (2 litre) containing 524 g tetrapropenylphenol (2002 meq) and 520 g n-hexane a solution of 67.5 g S_2Cl_2 (1000 meq of sulphur) in 70 g n-hexane was added dropwise at such a rate that the temperature was kept constant at 20-40 °C. When the S_2Cl_2 addition was complete (2-3 hrs) the reaction mixture was rinsed with nitrogen and the solvent removed under reduced pressure (yield: 557 g; S: 5.0 %w) (Product B).

These Examples show that sulphurization with elemental sulphur as well as with S_2Cl_2 is feasible.

Example 3

The product from example 2 was diluted with 500 g of xylene and then heated to 135 °C in a nitrogen atmosphere. An aqueous solution of 100 g sodium hydroxide (25 % excess on OH intake) in 120 g water was added carefully (to prevent foaming) and water was distilled off. The solution was carboxylated at 140 °C and 14 bar CO_2 pressure. After acidification and water wash the yield was 587 g of sulphurized salicylic acids, acid number 1.98 meq/g and sulphur content 4.72 %w (Product C).

Example 4

A solution of 200 g of the sulphurized alkylsalicylates of example 3 (396 meq) in 200 g of xylene and 120 g of methanol was treated with 59 g of $Ca(OH)_2$ (1595 meq) for 1h at 55 °C. The reaction product was filtered and the solvents were evaporated under reduced pressure resulting in a product (223 g) with 6.8 %w Ca, 3.9 %w S and a B.I. of 1.5 (Product D).

Example 5

A solution of 200 g of the sulphurized alkylsalicylates of example 3 (396 meq) in 200 g of xylene and 120 g of methanol was treated with 59 g of $Ca(OH)_2$ (1595 meq) for 1h at 55°C. Subsequently 13.9 g of CO_2 (632 meq) was introduced. Workingup yielded 253.5 g of a product with 11.5%w Ca, 3.7 %w S and a B.I. of 3.0 (Product E).170 g of product E was mixed with 155 g of mineral lubricating oil, resulting in an oil concentrate with 6.0 %w Ca, 1.9 %w S and a B.I. of 3.0 (product F).

Comperative Experiment

To 97.6 g (205 meq) of neat C_{14-18} alkyl salicylic-acids were added 37.9 (1025 meq) of $Ca(OH)_2$ and 69.5 g of a mineral lubricating oil, resulting in a 1.0 meq/g mixture of acids. 133.2 g of this mixture (133.2 meq), 4.26 g of S (133.2 meq) and 1.0 g of ethylene glycol were heated under stirring to 125 °C and kept at that temperature for one hour. The temperature was further raised to 150 °C (1 hour, pressure: 550 mm Hg) and 195 °C (2 hours, 50-60 mm Hg). The reaction mixture was cooled, diluted with n-hexane, filtered through filter aid and finally evaporated to yield a very viscous, dark material. Yield: 112.3 g, S: 1.6 %w.

It appeared that during the sulphurization 20% decarboxylation occurred (acid number of starting material 1.22 meq/g and of product 0.95 meq/g, determined after acidification with HCl extraction with diethyl ether, phase separation and evaporation of the solvent).

TESTS

In two CRC L38 tests (ASTM STP 509 A, part IV) the performance of product F (see Example 5) was compared with that of unsulphurized overbased Ca C_{14-18}-alkyl salicylate. Thereto two formulations were prepared, formulation I comprising a 15W40 mineral lubricating oil containing commercial dispersant, detergent and anti-oxidant additives and 0.14 %w (as Ca) of overbased Ca C_{14-18}-alkyl salicylate (B.I. = 3), and formulation II comprising the same 15W40 lubricating oil and 0.14 %w (as Ca) of product F. The results of the CRC L38 tests, in which the bearing weight loss is determined, are shown in Table I.

TABLE I

Formulation	I	II
Bearing weight loss, mg	45.4	29.6
" " " "	45.7	36.7

It appears that use of the sulphurized product of the invention results in a reduction of the bearing weight loss.

CLAIMS

1. Process for the preparation of a sulphurized, metal aliphatic hydrocarbon-substituted salicylate, characterized in that an aliphatic hydrocarbon-substituted phenol is sulphurized, and the resulting product is transformed into an alkali metal salicylate with an alkali metal hydroxide and carbon dioxide.

2. Process according to claim 1, wherein the alkali metal salicylate is transformed into the corresponding salicylic acid which is converted with a basic alkaline earth metal compound and carbon dioxide into an overbased alkaline earth metal salicylate.

3. Process according to claim 1 or 2, wherein the aliphatic hydrocarbon-substituted phenol is a C_{8-30}-alkylphenol.

4. Process according to any one of claims 1-3, wherein the sulphurization is carried out with a sulphur halide.

5. Process according to any one of claims 1-4, wherein the molar ratio of S:substituted phenol is 0.25 to 3.

6. Process according to any one of claims 1-5, wherein the product before or after sulphurization is reacted with a boron compound.

7. Product whenever prepared according to any one of claims 1-6.

8. Oil composition, in particular lubricating oil composition or concentrate or fuel, comprising an oil and 0.001-65 %w of a product as claimed in claim 7.

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EUROPEAN SEARCH REPORT

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Application number

EP 85201084.2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	GB - A - 825 315 (SOCONY MOBIL OIL COMPANY) * Claims 1,11,15,16; pages 3,4 * --	1-5,7,8
D,A	GB - A - 1 287 812 (THE LUBRIZOL CORPORATION) * Pages 1,2; claims * --	1,8
D,A	GB - A - 1 194 503 (THE LUBRIZOL CORPORATION) * Claims * --	1,8
D,A	GB - A - 786 167 (SHELL RESEARCH LIMITED) * Pages 1,2 * --	1,8
A	DE - A1 - 2 937 294 (MITSUI TOATSU CHEMICALS) * Claim 1 * --	1,4
A	GB - A - 1 443 329 (EXXON RESEARCH AND ENGINEERING COMPANY) * Claims 1,12,13 * --	1,4,8
A	US - A - 3 595 790 (GEORGE R. NORMAN et al.) * Claim 1; column 4, line 2 * --	1,8

CLASSIFICATION OF THE APPLICATION (Int Cl 4)
C 07 C 149/40 C 10 M 135/30

TECHNICAL FIELDS SEARCHED (Int Cl 4)
C 07 C 149/00 C 07 C 148/00 C 07 C 143/00 C 10 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	11-10-1985	REIF

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
A	US - A - 2 311 931 (ELMER WILLIAM COOK et al.) * Claims; example * --	1,2,4,8	
A	US - A - 2 319 662 (ELMER W. COOK et al.) * Claims 1-4; example 1 * --	1,2,3,8	
A	US - A - 2 335 017 (JOHN G. NC NAB et al.) * Claims * --	1,3,8	
A	US - A - 2 336 074 (ELMER W. COOK et al.) * Claims; example * --	1,4,8	TECHNICAL FIELDS SEARCHED (Int. Cl 4)
A	US - A - 4 212 752 (ANDREA PEDITTO et al.) * Page 1 * ----	1,2,8	

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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document