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(54) Process for the preparation of sulphurized overbased salicylates.

(57) Process for the preparation of sulphurized overbased metal aliphatic hydrocarbon-substituted salicylates by sulphurization of an aliphatic hydrocarbon-substituted salicylic acid or a metal salt thereof with a sulphur halide, and subsequently by transforming the reaction product into an overbased metal salicylate.

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PROCESS FOR THE PREPARATION OF SULPHURIZED OVERBASED SALICYLATES

This invention relates to a process for the preparation of sulphurized overbased metal aliphatic hydrocarbon-substituted salicylates by sulphurization of an aliphatic hydrocarbon-substituted salicylic acid or a metal salt thereof, 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 with elemental sulphur.

It has now been found that a much lower degree of decarboxylation can be obtained by reaction with a sulphur halide instead of with elemental sulphur.

This invention therefore relates to a process for the preparation of sulphurized overbased, metal aliphatic hydrocarbon-substituted salicylates by sulphurization of an aliphatic hydrocarbon-substituted salicylic acid or a metal salt thereof with a sulphur halide, and subsequently by transforming the reaction product into an overbased metal salicylate.

The invention furthermore relates to the products thus prepared and to oil compositions containing them. Suitable metals of the overbased metal salicylates 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.

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

As metal salt of the aliphatic hydrocarbon-substituted salicylic acid an alkali metal salt, in particular the sodium salt, is preferred.

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. Preferred sulphur halides are sulphur chlorides, such as SCl_2 and S_2Cl_2.

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

The molar ratio of S: substituted salicylic acid or salicylate is e.g. 0.25 to 3 preferably 0.5 to 2.

The reaction mixture may then be acidified, if necessary, to obtain the free sulphurized acid and filtered if desirable.

The product is used for the preparation of the corresponding overbased salicylates which combine good detergency with reduced wear in lubricating oil compositions.

The overbasing step can be carried out by reacting the resulting product in a solvent, such as a hydrocarbon solvent, preferably an aromatic hydrocarbon solvent, such as xylene, with a basic metal compound, preferably a hydroxide, and carbon dioxide, as described in e.g. British patent specification 786167. The degree of overbasing is expressed as the basicity index (B.I.), defined as the equivalent ratio of metal: salicylic acid.

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

To 500 g of a concentrate of 65 %w Na salt of C_{14-18} alkylsalicylic acids (600 meq acid, acid number 1.20 meq/g), in 35 %w mineral lubricating oil were added drop-wise 360 meq (30 g) S_2Cl_2 at about 25 °C. Total reaction time of addition and after-reaction 5 h. The reaction product was acidified with concentrated HCl, extracted with diethylether, and after phase-separation filtrated, whereafter the solvents were removed by evaporation. Yield 491 g, S:3.4 %w, acid number 1.24 meq/g (Product A).

Comparative Experiment 1

To 500 g of a concentrate of the Na salt of C_{14-18} alkylsalicylic acids of Example 1 were added 590 meq (19 g) S and 4 g ethylene glycol. The mixture was heated under stirring to 125 °C and kept at that temperature during 1 h. The temperature was then raised to 150 °C and kept at that temperature for one hour at a pressure of about 550mm Hg. Then the temperature was raised to 195 °C and the pressure lowered to 50-60 mm Hg, these conditions were maintained for two hours. The reaction product was then allowed to cool to about 100 °C before filtering through filter aid, to yield 554 g of product (Product B), having an S-content of 2.9 %w and an acid number of 0.39 meq/g.

Conclusion: compared with S_2Cl_2 the reaction with S resulted in a considerable degree of decarboxylation.

EXAMPLE 2

To 100 meq (51.8 g) neat C_{14-18} alkylsalicylic acids (acid number 1.93 meq/g) were added 60 meq (4 g) S_2Cl_2 in 6 ml n-hexane at about 25 °C according to Example 1. The reaction product was washed with water, and after phase-separation the solvents were removed by evaporation. Yield 52.2 g, S:3.5 %w, acid number 1.96 meq/g (Product C).

Comparative Experiment 2

To 193 meq (100 g) neat C_{14-18} alkylsalicylic acids of Example 3 were added 193 meq (6.2 g) S and 193 meq (7.2 g) $Ca(OH)_2$ and 1.5 g ethylene glycol. The mixture was reacted according to Example 2. Yield 102 g, S:3.0 %w, acid number 1.45 meq/g (Product D).

Conclusion: compared with S_2Cl_2 the reaction with S resulted in a considerable degree of decarboxylation.

EXAMPLE 3

1855 g (3636 meq) of the sulphurized C_{14-18} alkylsalicylic acids of Example 3 were diluted with 6280 g of xylene and 808 g of methanol. This mixture was reacted with 188.3 g (5090 meq) of $Ca(OH)_2$ for 1 h at 55 °C. The reaction product was centrifuged, 1500 g of mineral lubricating oil was added and the solvents were evaporated yielding 3775 g of an oil concentrate with 2.8 %w Ca and a B.I. of 1.27 (Product E).

EXAMPLE 4

A solution of 200 g (392 meq) of the sulphurized C_{14-18} alkylsalicylic acids of Example 3 in 400 g of xylene and 60 g of methanol was treated with 60 g (1622 meq) of $Ca(OH)_2$ for 1 h at 55 °C. Subsequently 14.0 g of CO_2 (633 meq) was introduced. Work up yielded 253.6 g of a product with 8.53 %w Ca, 2.72 %w S and a B.I. of 2.6 (Product F).

EXAMPLE 5

A solution of 500 g (980 meq) of the sulphurized C_{14-18} alkylsalicylic acids of Example 3 in 1000 g of xylene and 150 g of methanol was treated with 345 g (9310 meq) of $Ca(OH)_2$ for 1 h at 55 °C. Subsequently 151 g of CO_2 (6860 meq) was introduced. Work up yielded 840 g of a product with 18.08 %w Ca, 1.80 %w S and a B.I. of 7.9 (Product G).

CLAIMS

1. Process for the preparation of sulphurized overbased metal aliphatic hydrocarbon-substituted salicylates by sulphurization of an aliphatic hydrocarbon-substituted salicylic acid or a metal salt thereof, with a sulphur halide and subsequently by transforming the reaction product into an overbased metal salicylate.

2. Process according to claim 1, wherein the metal of the overbased metal salicylate is an alkaline earth metal.

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

4. Process according to any one of claims 1-3, wherein the molar ratio of S : substituted salicylic acid or salicylate is 0.25 to 3.

5. Process according to any one of claims 1-4, wherein the product before or after sulphurization is reacted with a boron compound.

6. Product whenever prepared according to any one of claims 1-5.

7. 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 6.

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EUROPEAN SEARCH REPORT

0168110
Application number

EP 85201082.6

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)
D,Y	GB - A - 1 287 812 (THE LUBRIZOL CORPORATION) * Pages 1,2; claims * --	1-3,7	C 07 C 149/40 C 10 M 135/30
D,Y	GB - A - 1 194 503 (THE LUBRIZOL CORPORATION) * Claims * --	1-3,7	
Y	GB - A - 825 315 (SOCONY MOBIL OIL COMPANY) * Claims 1,11,15,16; pages 3,4 * --	1,2,7	
D,A	GB - A - 786 167 (SHELL RESEARCH LIMITED) * Pages 1,2 * --	1,2,7	**TECHNICAL FIELDS SEARCHED (Int. Cl 4)**
A	US - A - 3 595 790 (GEORGE R. NORMAN et al.) * Claim 1 * --	1	C 07 C 148/00 C 07 C 149/00 C 07 C 143/00 C 10 M
A	US - A - 2 311 931 ELMER WILLIAM COOK et al.) * Claims * --	1,2,7	
A	US - A - 2 319 662 (ELMER W. COOK et al.) * Claims * --	1-3,7	

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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D : document cited in the application
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
A	<u>US - A - 2 335 017</u> (JOHN G. MC NAB et al.) * Claims * --	1,3,7	
A	<u>US - A - 2 336 074</u> (ELMER W. COOK et al.) * Claims * --	1-3,7	
A	<u>US - A - 4 221 673</u> (ROBERT ROBSON et al.) * Claims * --	1-3,7	
A	<u>US - A - 4 320 016</u> (BENJAMIN H. ZOLESKI et al.) * Page 1 * ----	1,2,7	
			TECHNICAL FIELDS SEARCHED (Int Cl 4)

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VIENNA	11-10-1985	REIF

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X : particularly relevant if taken alone
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