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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, wherein an aliphatic hydrocarbon-substituted salicylic acid is transformed into an over based metal salicylate having a basicity index of at least 1.5 by means of a basic metal compound and carbon dioxide and then the overbased metal salicylate is sulphurized by heating with elemental sulphur.

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, to products thus prepared and to oil compositions containing them.

5 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,
10 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
15 the disadvantage of a substantial degree of decarboxylation during the reaction with sulphur.

It has now been found that a much lower degree of decarboxylation can be obtained by reaction of the same type of aliphatic hydrocarbon-substituted salicylic acid, or the metal
20 salt thereof, with sulphur after overbasing with carbon dioxide, without loss of the excellent detergent and anti-wear properties.

This invention therefore relates to a process for the preparation of sulphurized overbased metal aliphatic hydrocarbon-substituted salicylates, characterized in that an aliphatic
25 hydrocarbon-substituted salicylic acid is transformed into an overbased metal salicylate having a basicity index of at least 1.5 by means of a basic metal compound and with carbon dioxide, and subsequently the overbased metal salicylate is sulphurized
30 by heating with elemental sulphur.

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

Suitable metals are e.g. alkali metals, such as Li, Cs, Na and K, alkaline earth metals, such as Ca, Ba, Sr and Mg, and
5 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 specifica-
10 tions. Preferred are C₈₋₃₀-alkyl salicylic acids.

The overbasing step can be carried out by reacting the hydrocarbon substituted salicylic acid in a solvent, such as a hydrocarbon solvent, preferably an aromatic hydrocarbon solvent, such as xylene, with a basic metal compound, preferably a
15 hydroxide, and carbon dioxide, as described in e.g. British patent specification 786167.

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.

20 The basicity index (BI) of the overbased salicylate, defined as the equivalent ratio of metal:salicylic acid, is at least 1.5, preferably at least 3 . It has been found that this is of importance in order to avoid any substantial amount of decarboxylation in the sulphurization step.

25 The sulphurization step can be carried out by contacting the resulting oil solution of the overbased salt with elemental sulphur, preferably in the presence of a solvent, at a temperature in the range of 100-250 °C, preferably 150-225 °C, whereby the final temperature should be at least 175 °C and preferably
30 at least 195 °C.

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.

The above-mentioned solvent of the sulphurization step pre-
35 ferably 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.

A promotor such as a 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 salicylic acid is e.g. 0.25 to 3, preferably 0.5 to 2.

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 C₁₃ 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

Overbased calcium C₁₄₋₁₈-alkyl salicylate, having a BI of 3 (Product A), was prepared from C₁₄₋₁₈-alkyl salicylic acid by means of calcium hydroxide and carbon dioxide, and was taken up in a mineral lubricating oil.

A reaction vessel (5 litre) was charged with 2500 g (2530 meq acid) of a concentrate of 67 %w of the overbased calcium C₁₄₋₁₈-alkyl salicylate in 33 %w of the mineral lubricating oil, 80 g (2500 meq) elemental sulphur and 20 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 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 give a dark viscous product (yield: 2500 g, S: 1.6 %w (Product B). It appeared that sulphurization at a lower temperature (175 °C) resulted in some dissolved unreacted sulphur, which is inclined to precipitate on standing.

It furthermore appeared that during the sulphurization only

a small amount of decarboxylation occurred (9%; acid number of starting material 1.06 and of product 0.96; acid number in meq acid/g, determined after acidification with HCl, extraction with diethyl ether, phase separation and evaporation of the solvent)
5 (same method in the following Examples).

Example 2

2500 g of a concentrate of 50 %w overbased calcium C_{14-18} -alkylsalicylate (1625 meq) prepared from the alkyl salicylic acids, calcium hydroxide and carbon dioxide and having a B.I. of
10 7.72, in 50 %w mineral lubricating oil was sulphurised with 51.3 g of elemental sulphur (1603 meq) and 13 g of ethylene glycol according to the process described in example 1. Yield: 2453 g, S: 1.2 %w.

It appeared that during sulphurisation 2% decarboxylation
15 occurred (acid number of starting material 0.79 meq/g and of product 0.77 meq/g).

Example 3

250 g of a concentrate of 62 %w overbased magnesium C_{14-18} -alkylsalicylate (213.5 meq) having a B.I. of 7.2 in 38 %w
20 mineral lubricating oil was sulphurised with 6.58 g of elemental sulphur (205.6 meq) and 1.7 g of ethylene glycol according to the process described in example 1. Yield: 243.6 g, S: 0.94 %w.

It appeared that during sulphurisation 3% decarboxylation occurred (acid number of starting material 1.02 meq/g and of
25 product 1.00 meq/g).

Comparative Experiment 1

To 97.6 g (205 meq) of neat C_{14-18} alkyl salicylic acids were added 37.9 g (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.
30 133.2 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,
35 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 %.

It appeared that during the sulphurisation 20% decarboxylation occurred (acid number of starting material 1.22 meq/g and
5 of product 0.95 meq/g).

Comparative Experiment 2

2500 g of a concentrate of 58 %w overbased calcium C₁₄₋₁₈-alkylsalicylate (2300 meq) having a B.I. of 1.28 in 42 %w mineral lubricating oil was sulphurised with 77 g elemental
10 sulphur (2406 meq) and 19 g of ethylene glycol according to the process described in example 1. Yield: 2496 g, S: 1.3 %w.

It appeared that during sulphurization 28% decarboxylation occurred (acid number of starting material 0.92 meq/g and of product 0.66 meq/g).

15 TESTS

In two 15W40 mineral lubricating oils (1 and 2), containing commercial dispersant, detergent and anti-oxidant additives, the products A and B (see Example 1) were tested.

Formulation I contained Product A in an amount of 0.14 %w
20 as Ca in lubricating oil 1. Formulation II contained lubricating oil 1 and 0.14 %w (as Ca) of Product B. Formulations III and IV comprised lubricating oil 2 with 0.19 %w as Ca of Product A and B, respectively.

Formulations I and II were tested in the CRC L38 test (ASTM
25 STP 509A, part IV) in which the bearing weight loss is determined. The results are represented in Table I:

TABLE I

Formulation	I	II
Bearing weight loss, mg	45.4	33.6

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

Formulations III and IV were tested in the MS Sequence IIID engine test in which the cam and lifter wear and cleanliness performance were determined.

The results are shown in Table II:

TABLE II

Test	1	2	3	4
Formulation	III	III	IV	IV
Maximum cam and lifter wear, mm	0.55	0.77	0.38	0.50
Average cam and lifter wear, mm	0.26	0.24	0.14	0.12
Average sludge rating (10 being clean)	9.66	9.58	9.63	9.58

- 5 It appears that use of the sulphurized products results in a reduction of the cam and lifter wear. The cleanliness rating remained about the same.

C L A I M S

1. Process for the preparation of sulphurized overbased metal aliphatic hydrocarbon-substituted salicylates, characterized in that an aliphatic hydrocarbon-substituted salicylic acid is transformed into an overbased metal salicylate having a basicity index of at least 1.5 by means of a basic metal compound and carbon dioxide, and subsequently the overbased metal salicylate is sulphurized by heating with elemental sulphur.
2. Process according to claim 1, wherein the metal is an alkaline earth metal.
- 10 3. Process according to claim 1 or 2, wherein the aliphatic hydrocarbon-substituted salicylic acid is a C₈₋₃₀-alkyl salicylic acid.
4. Process according to any one of claims 1-3, wherein the basicity index of the overbased salicylate is at least 3.
- 15 5. Process according to any one of claims 1-4, wherein the sulphurization is carried out at at least 175 °C.
6. Process according to any one of claims 1-5, wherein the molar ratio of S:substituted salicylic acid is 0.25 to 3.
7. Process according to any one of claims 1-6, wherein the product before or after sulphurization is reacted with a boron compound.
- 20 8. Product whenever prepared according to a process as claimed in any one of claims 1-9.
9. 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 8.
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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 85201083.4
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D,A	GB - A - 1 287 812 (THE LUBRIZOL CORPORATION) * Pages 1,2; claims 1,11,12 * --	1,2,9	C 07 C 149/40 C 10 M 135/30
D,A	GB - A 1 194 503 (THE LUBRIZOL CORPORATION) * Claims 1,17-20 * --	1,2,9	
D,A	GB - A - 786 167 (SHELL RESEARCH LIMITED) * Pages 1,2 * --	1,9	
A	GB - A - 825 315 (SOCONY MOBIL OIL COMPANY) * Claims 1,5,10,15,16; pages 3,4 * --	1-3,9	
A	US - A - 2 311 931 (ELMER WILLIAM COOK et al.) * Claims * --	1,2,9	C 07 C 148/00 C 07 C 149/00 C 07 C 143/00 C 10 M
A	US - A - 2 319 662 (ELMER W. COOK et al.) * Claims 1-4 * --	1-3,9	
A	US - A - 2 335 017 (JOHN G. MC NAB et al.) * Claims * --	1,2,9	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 11-10-1985	Examiner REIF
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



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Application number

EP 85201083.4

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>US - A - 2 336 074</u> (ELMER W. COOK et al.) * Claims * --	1,2,9	
A	<u>US - A - 4 212 752</u> (ANDREA PEDITTO et al.) * Page 1 * --	1,2,9	
A	<u>US - A - 4 221 673</u> (ROBERT ROBSON et al.) * Claims * --	1,2,9	
A	<u>US - A - 4 228 022</u> (WARREN LOWE et al.) * Abstract * --	1,2,9	
A	<u>US - A - 4 320 016</u> (BENJAMIN H. ZOLESKI et al.) * Page 1 * ----	1,2,9	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 11-10-1985	Examiner REIF
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			