

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) Publication number:

**0 168 110
B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **28.09.88**

(51) Int. Cl.⁴: **C 07 C 149/40,
C 10 M 135/30**

(71) Application number: **85201082.6**

(22) Date of filing: **04.07.85**

(54) **Process for the preparation of sulfurized overbased salicylates.**

(30) Priority: **06.07.84 GB 8417298**

(43) Date of publication of application:
15.01.86 Bulletin 86/03

(45) Publication of the grant of the patent:
28.09.88 Bulletin 88/39

(84) Designated Contracting States:
BE DE FR GB IT NL

(58) References cited:
**GB-A- 786 167
GB-A- 825 315
GB-A-1 194 503
GB-A-1 287 812
US-A-2 311 931
US-A-2 319 662
US-A-2 335 017
US-A-2 336 074
US-A-3 595 790
US-A-4 221 673
US-A-4 320 016**

(73) Proprietor: **SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR Den Haag (NL)**

(72) Inventor: **Heldeweg, Rudolf Frank
Badhuisweg 3
NL-1031 CM Amsterdam (NL)
Inventor: Booth, Martin
Badhuisweg 3
NL-1031 CM Amsterdam (NL)
Inventor: van Kruchten, Eugène Marie Godfried
Andre
Badhuisweg 3
NL-1031 CM Amsterdam (NL)**

(74) Representative: **Aalbers, Onno et al
P.O. Box 302
NL-2501 CH The Hague (NL)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

EP 0 168 110 B1

Description

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.

UK Patent Specification 825315, and USP. 2,335,017 and USP 2311931 disclose the reaction of sulphur chlorides with phenols and with unsubstituted salicylate esters. However, those phenols and esters are significantly more reactive than the hydrocarbon-substituted salicylic acids (or their metal salts) which form the starting materials for the production of overbased hydrocarbon-substituted salicylates used as lubeoil additives. Hence, it could not be predicted that sulphur halides would react with such starting materials. Surprisingly, according to the present invention, it has been found that sulphur halides can, indeed, be used in the sulphurization of hydrocarbon-substituted salicylic acids, and that the use of this reagent in place of the elemental sulphur hitherto employed results in a much lower degree of decarboxylation.

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 C₈₋₃₀-alkyl salicylic acids.

As metals 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 SCl₂ and S₂Cl₂.

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 acids 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

To 500 g of a concentrate of 65 %w Na salt of C₁₄₋₁₈ 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) S₂Cl₂ 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 C₁₄₋₁₈ 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 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 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 S₂Cl₂ the reaction with S resulted in a considerable degree of decarboxylation.

Example 2

To 100 meq (51.8 g) neat C₁₄₋₁₈ alkylsalicylic acids (acid number 1.93 meq/g) were added 60 meq (4 g) S₂Cl₂ 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 C₁₄₋₁₈ 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 S₂Cl₂ the reaction with S resulted in a considerable degree of decarboxylation.

Example 3

1855 g (3636 meq) of the sulphurized C₁₄₋₁₈ 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 C₁₄₋₁₈ 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 CO₂ (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 C₁₄₋₁₈ 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 CO₂ (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, and subsequently overbasing the product by reaction with a basic metal compound and carbon dioxide, characterised in that the sulphurization is effected by reaction with a sulphur halide.

2. Process as claimed in claim 1 wherein the sulphur halide is SCl₂ or S₂Cl₂.

3. Process according to claim 1 or 2, wherein the molar ratio of S: substituted salicylic acid or salicylate is 0.25 to 3.

4. Process according to any one of claims 1—3, wherein the metal of the overbased metal salicylate is an alkaline earth metal.

5. Process according to any one of claims 1—4, wherein the aliphatic hydrocarbon-substituted salicylic acid is a C₈₋₃₀-alkyl salicylic acid.

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

7. Oil composition, in particular lubricating oil

composition or concentrate or fuel, comprising an oil and 0.001—65 %w of a sulphurized overbased metal aliphatic hydrocarbon-substituted salicylate as produced by the process according to claim 1.

Patentansprüche

1. Verfahren zur Herstellung von sulfurierten überbasischen mit aliphatischen Kohlenwasserstoffgruppe(n) substituierten Metallsalicylaten durch Sulfurierung einer mit aliphatischen Kohlenwasserstoffgruppe(n) substituierten Salicylsäure oder eines Metallsalzes derselben und anschließendem Überbasisch-Machen des Produkts durch Umsetzung mit einer basischen Metallverbindung und Kohlendioxid, dadurch gekennzeichnet, daß die Sulfurierung durch Umsetzung mit einem Schwefelhalogenid erfolgt.

2. Verfahren wie in Anspruch 1 beansprucht, in welchem das Schwefelhalogenid SCl_2 oder S_2Cl_2 ist.

3. Verfahren nach Anspruch 1 oder 2, in welchem das molare Verhältnis von S: substituierter Salicylsäure oder Salicylat 0,25:1 bis 3:1 ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, in welchem das Metall des überbasischen Metallsalicylats ein Erdalkalimetall ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, in welchem die mit aliphatischen Kohlenwasserstoffgruppe(n) substituierte Salicylsäure eine C_{8-30} -Alkylsalicylsäure ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, in welchem das Produkt vor oder nach der Sulfurierung mit einer Borverbindung umgesetzt wird.

7. Ölzusammensetzung, insbesondere eine Schmierölszusammensetzung oder ein Konzentrat oder Brennstoff, enthaltend 0,001 bis 65 Gewichtsprozent eines sulfurierten überbasischen mit aliphatischen Kohlenwasserstoffgrup-

pe(n) substituierten Metallsalicylats, wie durch das Verfahren nach Anspruch 1 hergestellt.

Revendications

1. Procédé pour la préparation de sels métalliques surbasiques sulfurés d'acides salicyliques substitués par des hydrocarbures aliphatiques par sulfuration d'un acide salicylique substitué par un hydrocarbure aliphatique ou d'un sel de métal d'un tel acide, et transformation ensuite du produit en un composé surbasique par réaction avec un composé basique de métal et l'anhydride carbonique, caractérisé en ce que la sulfuration est effectuée avec un halogénure de soufre.

2. Procédé selon la revendication 1, dans lequel l'halogénure de soufre est SCl_2 ou S_2Cl_2 .

3. Procédé selon la revendication 1 ou 2, dans lequel le rapport molaire de S à l'acide salicylique ou au salicylate substitué est de 0,25 à 3.

4. Procédé selon l'une quelconque des revendications 1—3, dans lequel le métal du salicylate métallique surbasique est un métal alcalino-terreux.

5. Procédé selon l'une quelconque des revendications 1—4, dans lequel l'acide salicylique substitué par un hydrocarbure aliphatique est un acide C_{8-30} -alcoyl salicylique.

6. Procédé selon l'une quelconque des revendications 1—5, dans lequel le produit avant ou après la sulfuration est mis à réagir avec un composé du bore.

7. Composition d'huile, en particulier composition d'huile lubrifiante ou concentré ou combustible, comprenant une huile et 0,001—65% en poids d'un sel métallique surbasique sulfuré d'acide salicylique substitué par un hydrocarbure aliphatique tel que produit par le procédé selon la revendication 1.

5

10

15

20

25

30

35

40

45

50

55

60

65

4