

PRODUCTION OF STABILIZED AND DEODORIZED ORGANIC
POLYSULPHIDES

The present invention relates to organic polysulphides, and more particularly to the manufacture of stabilized and deodorized organic polysulphides.

5 Organic polysulphides, which can typically be represented by the general formula RS_nR' in which n is an integer of from 2 to 15 and R and R' are substituted or unsubstituted hydrocarbyl radicals, are used in numerous applications such as, for example, presulphurization of
10 hydrorefining catalysts and addition to elastomers. They are also excellent extreme-pressure and anti-wear additives for lubricants, and are therefore involved in the composition of lubricating formulations for gearboxes and for machining metals. Most applications require a
15 polysulphide which is odourless, precipitate-free, clear and stable in the long-term.

 However, organic polysulphides are generally prepared by reacting a mercaptan with elementary sulphur in the presence of a basic catalyst; they may also be
20 prepared from an olefin, sulphur and/or hydrogen sulphide, optionally in the presence of a basic catalyst. Products prepared in this way contain or release hydrogen sulphide and/or mercaptans, which are difficult to remove.

25 Hydrogen sulphide is toxic and, together with mercaptans, causes unpleasant odours. Furthermore if catalytic residues are present, the residual mercaptan and hydrogen sulphide make the finished product unstable, leading to some degree of turbidity or the appearance of
30 precipitates in the course of time.

 In order to deodorize and stabilize organic polysulphides, it is essential to remove the mercaptan and hydrogen sulphide residues by suitable treatment. Various processes for solving this problem have already
35 been described:

- washing the raw polysulphide with an acid and/or base solution (US Patent 5 155 275);
- washing the raw polysulphide with an oxidizing solution in the presence of a catalytic amount of base (US Patent 5 206 439);
- washing the raw polysulphide with an alcoholic or aqueous solution of a metal salt (US Patent 5 403 961);
- treating the raw polysulphide with an acid and subsequent distillation (US Patent 5 530 163);
- treating the raw polysulphide with an alkene oxide in the presence of a catalytic amount of base (Japanese patent specification JP 58-140063 and US patent 5 218 147).

These processes are not entirely satisfactory. The washing processes require the addition of solvents or aqueous solutions which are difficult to separate from the polysulphide at the end of the treatment, unless time-consuming and expensive separation means are employed. The process involving final distillation is expensive in terms of energy and is applicable only to light polysulphides. Alkene oxides are toxic and carcinogenic.

Some methods do not make it possible, in a single treatment, to reduce the residual mercaptan sulphur level to a level which is low enough to stabilize the polysulphide; the need to carry out several successive treatments makes these time-consuming and expensive methods.

A process has now been found for stabilizing polysulphides and reducing the residual mercaptan level, which is fast, uses reactants which are not very toxic and does not require the use of a solvent or phase mixture, or distillation.

According to the present invention there is

provided a process for preparing a stabilized and deodorized organic polysulphide, which process comprises treating a raw organic polysulphide with an alkylene carbonate in the presence of a basic catalyst and, optionally, a sulphur donor.

The present invention will now be described in detail.

a - Polysulphide treated according to the invention

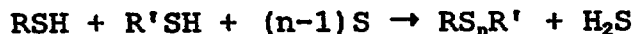
The organic polysulphide treated according to the present invention typically satisfies the general formula RS_nR' in which n is from 2 to 15 and each of R and R' , which may be the same or different, is generally a hydrocarbyl radical having 1 to 20 carbon atoms which may be saturated or comprise one or more unsaturations. These radicals are generally alkyl, cycloalkyl or aryl radicals; the alkyl or cycloalkyl radicals may be substituted by formyl or acyl ($-COR''$), carboxyl or carboxylic ester ($-COOR''$), carbonitrile, azomethine ($-CR''=NR'''$), carboxamide ($-CONR''R'''$), nitro, hydroxyl, alkoxy, amino ($-NR''R'''$) or $-SiR'''$, functional groups, or by aryl or cycloalkyl groups, each of R'' and R''' , which may be the same or different, representing a hydrogen atom or an alkyl radical, and the three substituents R''' , which may be the same or different, being alkyl or alkoxy radicals. Preferably, R and R' are alkyl radicals, which may be branched or unbranched, having 4 to 12 carbon atoms and n is from 3 to 6.

The organic polysulphide may also be the product of sulphurization of an olefin, a polyolefin, a polyunsaturated olefin, a fatty oil, a fatty ester or a fatty acid. Sulphurized olefins comprise products made by sulphurizing an olefin (for example isobutylene) or a polyolefin (for example diisobutylene) with sulphur, sulphur chloride, sulphur dichloride or hydrogen

5 sulphide, or a combination of these products, optionally
in the presence of a basic catalyst. The oils which may
be sulphurized are natural or synthetic oils comprising
mineral oils, lard oils, carboxylic esters derived from
aliphatic alcohols and fatty acids or aliphatic
10 carboxylic acids, and unsaturated esters or glycerides.
The fatty acids generally contain from 8 to 30 carbon
atoms and are, for example, palmitoleic, oleic,
ricinoleic, linoleic, oleostearic acid, etc. The
15 sulphurized fatty acid esters may also be prepared from
mixtures of fatty acid esters such as those obtained from
animal fats or vegetable oils.

b - Raw polysulphide and mode of preparation
(processes which are already known)

15 The raw organic polysulphide treated according
to the present invention may be prepared by a wide
variety of processes. One preparation method known in the
prior art comprises reacting one or more mercaptans with
elementary sulphur in the presence of a basic catalyst
20 according to the following reaction:



Processes for preparing organic polysulphides
according to this method are described, for example, in
US Patents US 2 237 625, US 3 022 351, US 3 038 013, US 3
25 392 201, US 4 564 709, US 5 206 439 and US 5 530 163;
French patent specifications FR 1 381 625, FR 1 553 249,
FR 2 607 496 and FR 2 635 775; European patent
specifications EP 25944 and EP 337837; and International
patent specifications WO 97/21649 and WO 97/21673.

30 The raw organic polysulphide may also be
produced by sulphurizing an olefin, polyolefin, fatty
oil, fatty ester or fatty acid, using the processes
described, for example, in US Patents US 4 937 385,
US 5 242 613 and US 5 250 737; European patent
35 specification EP 201197; and International patent

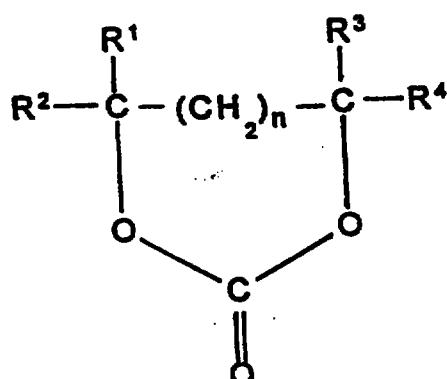
specifications WO 92/3524 and WO 92/397.

At the end of the reaction leading to the production of the raw polysulphide, the hydrogen sulphide contained in the raw product may be partly removed by degassing, in particular by bubbling an inert gas (advantageously nitrogen, air or methane, etc.), vacuum evaporation or any other method known in the art.

c - Treatment according to the invention of the raw polysulphide

According to the present invention, the raw polysulphide is treated with an alkylene carbonate in the presence of a basic catalyst and, optionally, a sulphur donor.

The alkylene carbonate used in the present invention may be ethylene carbonate, propylene carbonate, butylene carbonate or trimethylene carbonate, and more generally any compound of formula:



in which n is 0, 1 or 2 and each of R¹, R², R³ and R⁴, which may be the same or different, represents a hydrogen atom or an alkyl radical. The preferred alkylene carbonate is ethylene carbonate, a reactant which is inexpensive and not very toxic, its LD₅₀ (oral, rat) being equal to 10.4 g/kg.

The amount of alkylene carbonate to be used depends on the quantity of mercaptan(s) and hydrogen sulphide in the raw polysulphide. A mass ratio of alkylene carbonate relative to the raw polysulphide

of from 0.001:1 to 0.2:1, and preferably 0.005:1 to 0.1:1 will generally be used.

Advantageously, if the quantity of mercaptan(s) and H₂S remaining in the raw polysulphide is known, a
5 molar ratio of alkylene carbonate relative to the sum of the molar quantities of mercaptan(s) and H₂S will be used which is between 0.5:1 and 10:1, preferably between 0.9:1 and 2.5:1.

Non-limiting examples of basic catalysts usable
10 in the process according to the invention which may be mentioned are:

- amines (such as triethylamine or any other primary, secondary or tertiary amine), ammonium hydroxides, alkanolamines,
- 15 - mercaptides or alcoholates such as R⁵SNa, R⁵ONa, calcium or barium phenoxide, the compounds R⁵O(CH₂CH₂O)_mNa, R⁵S(CH₂CH₂O)_mNa or a catalyst comprising a mercaptan and an alkenoxide with an alkaline base (see French patent specification FR 2 607 496, the content of
20 which is incorporated here by reference), wherein R⁵ is an alkyl or cycloalkyl radical and m is an integer from 1 to 15,
- metal hydroxides such as LiOH, NaOH and KOH,
- metal oxides or metal salts such as Na₂O,
25 K₂O, MgO, NaHCO₃, Na₂CO₃ and CaCO₃), which may be used as they are or fixed on a support (for example an alumina or a silica),
- zeolites or hydrotalcites,
- aluminas, titanates, silicas or mixtures of
30 these compounds, optionally modified by alkalis or alkaline-earth bases, and
- basic anion-exchange resins such as, for example, resins based on styrene/divinylbenzene copolymer functionalized by primary, secondary or tertiary amine,
35 quaternary ammonium, guanidine, amidine groups or a

combination of these groups.

The catalyst may be used as it is or in the presence of a solvent such as water, an alcohol, carbon disulphide or any other suitable solvent.

5 The basic catalyst of the present invention may already be contained in the raw polysulphide. This is the case, in particular, when the reaction by which the raw polysulphide is synthesized uses a basic catalyst which is not separated from the raw polysulphide. The basic
10 catalyst of the present invention may also be added to the raw polysulphide.

 The amount of basic catalyst may vary within wide limits. Generally, the catalyst is used in an amount of from 0.001% to 50% relative to the weight of raw
15 polysulphide, and preferably 0.05% to 25%.

 Preferably, the basic catalyst used comprises a mercaptan and an alkene oxide with an alkaline base, or an anion-exchange resin. In the former case, the amount of catalyst is advantageously from 0.001 to 10%
20 (preferably 0.05 to 2%) relative to the weight of raw polysulphide. When an anion-exchange resin is used, this amount is advantageously from 0.1 to 50% (preferably 1 to 25%) relative to the weight of raw polysulphide.

 The process according to the invention may be
25 carried out in any suitable equipment. It is advantageously the equipment used for preparing the raw polysulphide. After the alkylene carbonate, and optionally the basic catalyst, has been added to the raw polysulphide (or vice versa), the mixture is stirred at a
30 temperature of about 15 to 150°C (preferably 50 to 120°C) for a period of from 2 minutes to 10 hours (preferably from 5 minutes to 5 hours).

 In certain cases (in particular for certain trisulphides such as di-t-dodecyl trisulphide or di-t-nonyl trisulphide) and if the alkylene carbonate on its
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own does not allow the residual mercaptan level to be reduced fast enough, it may be advantageous to use a certain amount of a sulphur donor in synergy with the alkylene carbonate.

5 The sulphur donor may be sulphur (in any form: liquid, bead, powder, etc.) or an organic polysulphide having 4 or more sulphur atoms per molecule. The preferred sulphur donors are sulphur, di-t-dodecyl pentasulphide and di-t-nonyl pentasulphide.

10 If the sulphur donor used is sulphur, a mass ratio of sulphur donor relative to the raw polysulphide of from 0:1 to 0.2:1 (preferably 0:1 to 0.1:1) will generally be used. If the sulphur donor used is an organic polysulphide, a mass ratio of sulphur donor
15 relative to the raw polysulphide of from 0:1 to 1:1 (preferably 0:1 to 0.2:1) will generally be used.

 The sulphur donor may be added before, at the same time as or even after the catalyst and the alkylene carbonate. Addition of the sulphur donor and alkylene
20 carbonate simultaneously is preferred. The mixture is stirred at a temperature of about 15 to 150°C (preferably 50 to 120°C) for a period of from 2 minutes to 10 hours (preferably 5 minutes to 5 hours).

 The finished product may then be purified if
25 necessary. This can be done using the conventional separation methods such as distillation or filtration.

 The process of this invention may also be adapted for continuous production.

 As it has been described, the process of this
30 invention has the effect of reducing the level of residual mercaptan and H_2S to a level low enough for the polysulphide to be deodorized and stabilized.

 The following examples illustrate the invention without limiting it. Unless otherwise indicated, the
35 percentages given are percentages by mass.

EXAMPLE 1: Preparation of di-t-dodecyl polysulphide having on average 5 sulphur atoms - finishing with ethylene carbonate by homogeneous catalysis

5 8.08 kg of t-dodecyl mercaptan and 60.6 g of a liquid catalyst obtained by reacting t-dodecyl mercaptan, ethylene oxide and sodium hydroxide according to the process described in French patent specification FR 2 607 496 were introduced into a 28 litre stainless
10 steel reactor connected to a flare. 2.5 kg of solid sulphur were added over a period of one hour to the mixture which was heated to 90°C and stirred continuously. Substantial release of H₂S gas took place and, after 30 minutes, a strong flow of methane (200 l/h)
15 was passed through the mixture for one and a half hours in order to remove the majority of the residual H₂S.

At the end of this operation, the raw polysulphide obtained contains 0.25% of mercaptan sulphur (determined by potentiometric titration using AgNO₃),
20 which corresponds to 98% conversion of the initial mercaptan.

80 g of ethylene carbonate (corresponding to 1.2 mol equivalents relative to the residual mercaptan) is added to the same reactor in a single operation at
25 90°C. Significant release of gas takes place. After one and a half hours of stirring at 90°C, the mixture is cooled and filtered to give 9.9 kg of finished product (more than 99% yield). Analysis of the finished product shows a mercaptan sulphur content of less than 10 ppm.
30 The product is stable, did not contain H₂S, and no precipitate appears after 3 months.

EXAMPLE 2: Preparation of di-t-dodecyl polysulphide having on average 5 sulphur atoms - finishing with ethylene carbonate by heterogenous catalysis

5 A mixture of 8.08 kg of t-dodecyl mercaptan and 808 g of Amberlyst® A21 ion-exchange resin (marketed by Röhm and Haas) is heated to 90°C while being stirred in a 28 litre stainless steel reactor connected to a flare. 2.56 kg of sulphur in bead form are then introduced over
10 a period of one hour. A substantial amount of H₂S gas is released and is disposed of in the flare. After 30 minutes, a flow of methane (200 l/h) is passed through the mixture for two and a half hours, in order to remove the majority of the residual H₂S.

15 At the end of this operation, the raw polysulphide obtained contains 0.32% of mercaptan sulphur, which corresponds to 97.6% conversion of the mercaptan introduced.

20 A 50 g sample of this raw polysulphide taken without catalyst is introduced into a cooled 100 ml three-necked flask. 5 g of Amberlyst® A21 resin and 0.52 g of ethylene carbonate (EC) are added thereto at 60°C. After stirring for two hours at this temperature, the mercaptan sulphur level is less than 10 ppm and the
25 finished product does not contain H₂S. The product is stable over time (test 2 in Table 1).

EXAMPLE 3: Comparative

30 The raw polysulphide (50 g) described in Example 2 is heated to 90°C in the presence of A21 resin without ethylene carbonate. After 2 hours, the residual mercaptan sulphur level is 1200 ppm and is not stable (test 3 in Table 1).

 The raw polysulphide (50 g) described in Example 2 is heated to 90°C without resin in the presence

of 0.52 g of ethylene carbonate. After 2 hours at 60 or 90°C, the residual mercaptan level is still 3200 ppm (test 4 in Table 1).

TABLE 1
Finishing of di-t-dodecyl polysulphide
 (mercaptan sulphur level before reaction: 3200 ppm)

Test	Resin catalyst	Reactant	mol ratio of reactant relative to residual mercaptan	Duration	Temperature	Mercaptan sulphur level after the reaction
2	A21	EC	1.5	2 h	60°C	10 ppm
3	A21	none	0	2 h	90°C	1200 ppm
4	none	EC	1.5	2 h	90°C	3200 ppm

EXAMPLE 4: Preparation of di-t-butyl trisulphide

A mixture of 135 g of t-butyl mercaptan (TBM) and 1.69 g of the liquid catalyst described in Example 1 is heated to 65°C in a 500 ml glass reactor fitted with a cooler to 0°C. 43.5 g of solid sulphur are then added over a period of 35 minutes and under vigorous stirring. The stirring is continued at this temperature for 90 minutes, then the temperature is increased to 100°C and nitrogen is passed through the reaction mixture with vigorous stirring for 120 minutes.

At this stage, the residual mercaptan sulphur level in the raw polysulphide is 1.27%, which corresponds to a TBM level of 3.5% by mass.

The raw polysulphide is then treated with 7.7 g of ethylene carbonate at 90°C. Substantial release of gas takes place, and this ceases after 30 minutes. Nitrogen is then passed through the mixture with vigorous stirring. After 2 hours at 90°C, the product is filtered. A limpid, virtually odourless liquid is obtained which is stable over time and in which the residual mercaptan sulphur level is less than 15 ppm.

EXAMPLE 5: Comparative

The raw polysulphide obtained in Example 4 is heated for two and a half hours at 90°C under the same conditions as in Example 4, with nitrogen being passed through but without ethylene carbonate. The mercaptan sulphur level remains high (2600 ppm) and the product obtained has a foul smell.

EXAMPLE 6: Preparation of di-t-dodecyl trisulphide

404 g of t-dodecyl mercaptan and 5 g of the liquid catalyst described in Example 1 are introduced

into a 1 litre glass reactor. The mixture is heated to 110°C and stirred continuously. 60.8 g of sulphur powder are then introduced over a period of 15 minutes. A substantial amount of H₂S gas is released. After
5 20 minutes, a strong flow of nitrogen is passed through the mixture for one hour, in order to remove the majority of the H₂S.

After this operation, the raw polysulphide obtained contains 1.51% of mercaptan sulphur (determined
10 by potentiometric titration using AgNO₃), corresponding to 90% conversion of the initial mercaptan. :

19.5 g of ethylene carbonate (corresponding to 1.08 mol equivalents relative to the residual mercaptan) mixed with 9.6 g of sulphur powder were added to the same
15 reactor in a single operation at 110°C. A significant amount of gas is released. After one and a half hours of stirring at 110°C, the mixture is cooled and filtered. Analysis of the finished product shows a mercaptan sulphur level of less than 9 ppm. The product is stable,
20 does not contain H₂S and no precipitate appears after 3 months.

EXAMPLE 7: Comparative

The raw polysulphide of the previous example is treated at 110°C with 27.5 g of ethylene carbonate
25 (corresponding to 1.5 mol equivalents relative to the residual mercaptan) without adding any sulphur donor. Very little gas is released.

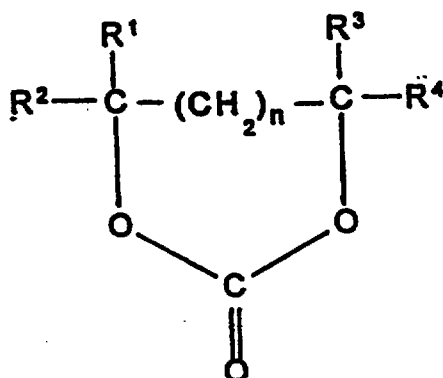
After 10 hours of stirring at this temperature with appreciable nitrogen stripping, the residual
30 mercaptan sulphur level is still more than 0.5% and the product is not stable.



CLAIMS

1. A process for preparing a stabilized and deodorized organic polysulphide, which process comprises treating a raw organic polysulphide with an alkylene carbonate in the presence of a basic catalyst.

2. A process according to Claim 1, in which the alkylene carbonate is a compound of formula



in which n is 0, 1 or 2 and each of R¹, R², R³ and R⁴, which may be the same or different, represents a hydrogen atom or an alkyl radical.

3. A process according to Claim 1 or 2, in which the alkylene carbonate is ethylene carbonate.

4. A process according to any one of Claims 1 to 3, in which the mass ratio of the alkylene carbonate to the raw polysulphide is between 0.001:1 and 0.2:1.

5. A process according to Claim 4, in which the mass ratio of the alkylene carbonate to the raw polysulphide is between 0.005:1 and 0.1:1.

6. A process according to any one of Claims 1 to 3, in which the molar ratio of the alkylene carbonate to the sum of the molar quantities of mercaptan(s) and hydrogen sulphide present in the raw polysulphide is between 0.5:1 and 10:1.

7. A process according to Claim 6, in which the molar ratio of the alkylene carbonate to the sum of



the molar quantities of mercaptan(s) and hydrogen sulphide present in the raw polysulphide is between 0.9:1 and 2.5:1.

5 8. A process according to any one of Claims 1 to 7, in which the basic catalyst is used in an amount of from 0.001 to 50% relative to the weight of raw polysulphide.

9. A process according to Claim 8, in which the basic catalyst is used in an amount of from 0.05 to 10 25% relative to the weight of raw polysulphide.

10. A process according to any one of Claims 1 to 9, in which the basic catalyst comprises a mercaptan and an alkene oxide with an alkaline base.

11. A process according to Claim 10, in which 15 the catalyst is used in an amount of from 0.001 to 10% relative to the weight of raw polysulphide.

12. A process according to Claim 11, in which the catalyst is used in an amount of from 0.05 to 2% relative to the weight of raw polysulphide.

13. A process according to any one of Claims 1 20 to 9, in which the basic catalyst is an anion-exchange resin.

14. A process according to Claim 13, in which the catalyst is used in an amount of from 0.1 to 50% 25 relative to the weight of raw polysulphide.

15. A process according to Claim 14, in which the catalyst is used in an amount of from 1 to 25% relative to the weight of raw polysulphide.

16. A process according to any one of Claims 1 30 to 15, in which the treatment is carried out at a temperature of from about 15 to 150°C.

17. A process according to Claim 16, in which the treatment is carried out at a temperature of from about 50°C to 120°C.



18. A process according to any one of Claims 1 to 17, in which the duration of the treatment is between 2 minutes and 10 hours.

19. A process according to Claim 18, in which the duration of treatment is between 5 minutes and 5 hours.

20. A process according to any one of Claims 1 to 19, in which the treatment is also carried out in the presence of a sulphur donor.

21. A process according to Claim 20, in which the sulphur donor is sulphur or an organic polysulphide having at least 4 sulphur atoms per molecule.

22. A process according to Claim 21, in which the sulphur donor is sulphur and a mass ratio of the sulphur to the raw polysulphide of from 0:1 to 0.2:1 is used.

23. A process according to Claim 22, in which the mass ratio of the sulphur to the raw polysulphide is from 0:1 to 0.1:1.

24. A process according to Claim 21, in which the sulphur donor is an organic polysulphide used in a sulphur donor/raw polysulphide mass ratio of from 0:1 to 1:1.

25. A process according to Claim 24, in which the sulphur donor is di-t-dodecyl or di-t-nonyl pentasulphide.

26. A process according to Claim 24 or 25, in which the sulphur donor/raw polysulphide mass ratio is from 0:1 to 0.2:1.

27. A process according to any one of Claims 1 to 26, in which the raw polysulphide is of formula RS_nR' in which each of R and R', which may be the same or different, represents an alkyl radical having 4 to 12 carbon atoms and n is from 3 to 6.



28. A process according to any one of Claims 3 to 19, in which the polysulphide is tert-nonyl or tert-dodecyl polysulphide, or tert-butyl trisulphide.

5 29. A process according to any one of Claims 20 to 26, in which the polysulphide is tert-dodecyl trisulphide.

30. A process according to Claim 1 substantially as described in any one of Examples 1, 2, 4 and 6.

10 31. A stabilized and deodorized organic polysulphide prepared by the process claimed in any one of the preceding claims.