618092

COMMONWEALTH of AUSTRALIA
Patents Act 1952

APPLICATION FOR A STANDARD PATENT

I/We

Rhone-Poulenc Sante

of

20 Avenue Raymond Aron, Antony, F-92160, France

hereby apply for the grant of a Standard Patent for an invention entitled:

Process for the preparation of cyclic sulphates

which is described in the accompanying complete specification.

Details of basic application(s):-

Number	Convention Country	Date
8806523	France	16 May 1988

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

DATED this FIFTEENTH day of MAY 1989

To: THE COMMISSIONER OF PATENTS

.....
a member of the firm of
DAVIES & COLLISON for
and on behalf of the
applicant(s)

Davies & Collison, Melbourne

M 009022 150589

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT

Insert title of invention.

In support of the Application made for a patent for an invention entitled: "Process for the preparation of cyclic sulphates"

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I Jacques PILARD, Executive of RHONE-POULENC SANTE of 20 avenue Raymond Aron, F-92160 Antony, France (formerly of "Les Miroirs", 18 avenue d'Alsace, F-92400 Courbevoie, France)

Cross out whichever of paragraphs 1(a) or 1(b) does not apply

1(a) relates to application made by individual(s)
1(b) relates to application made by company; insert name of applicant company.

do solemnly and sincerely declare as follows :-

1. (a) I am the applicant for the patent

or (b) I am authorized by RHONE-POULENC SANTE, a French Body Corporate of 20 avenue Raymond Aron, F-92160 Antony, France

the applicant..... for the patent to make this declaration on its behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply

2(a) relates to application made by inventor(s)
2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

2. (a) I am the actual inventor of the invention

or (b)

Viviane MASSONNEAU of Charrière Blanche, Pins 5, 69130 Ecully, France

Michel MULHAUSER of Résidence Charrière Blanche, "Immeuble Frènes 4", 69130 Ecully, France

BOTH FRENCH CITIZENS

is/are the actual inventor/s..... of the invention and the facts upon which the applicant..... is/are entitled to make the application are as follows :-

State manner in which applicant(s) derive title from inventor(s)

Employment Contract whereby the applicant would if a patent were granted on an application made by the said inventors, be entitled to have the patent assigned to it.

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act was/were made

in FRANCE NO. 8806523 on the 16TH MAY 1988

by RHONE-POULENC SANTE

in ..... on the .....

by.....

in ..... on the .....

by.....

4. The basic application..... referred to in paragraph 3 of this Declaration was/were the first application..... made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at Antony this 18th day of April 1989

Signature of declarant(s) (no attestation required)

RHONE-POULENC SANTE

BY: Jacques PILARD

Note: Initial all alterations.

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-34795/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 618092

(54) Title
PROCESS FOR THE PREPARATION OF CYCLIC SULPHATES

International Patent Classification(s)
(51)[4] C07D 327/10

(21) Application No. : 34795/89 (22) Application Date : 15.05.89

(30) Priority Data

(31) Number (32) Date (33) Country
88 06523 16.05.88 FR FRANCE

(43) Publication Date : 16.11.89

(44) Publication Date of Accepted Application : 12.12.91

(71) Applicant(s)
RHONE-POULENC SANTE

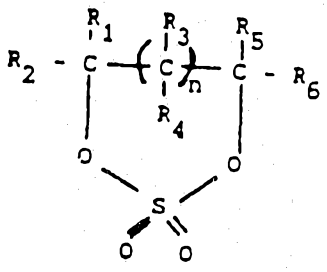
(72) Inventor(s)
VIVIANE MASSONNEAU; MICHEL MULHAUSER

(74) Attorney or Agent
DAVIES & COLLISON , 1 Little Collins Street, MELBOURNE VIC 3000

(56) Prior Art Documents
AU 31016/89 C07D 327/10

(57) Claim

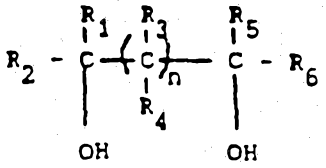
1. A process for the preparation of a cyclic sulphate of formula:



in which R_1, R_2, R_3, R_4, R_5 and R_6, which are identical or different, each denote a hydrogen or halogen atom or an alkyl, aryl, alkoxy, aryloxy or alkoxycarbonyl radical and n is 0 or 1, the aforesaid alkyl radicals and the alkyl moieties of the alkoxy and alkoxycarbonyl radicals containing 1 to 4 carbon atoms each and being unsubstituted or substituted by one or more identical or different atoms or radicals chosen from halogen atoms and alkoxy, aryloxy or alkoxycarbonyl radicals, and the said aryl radicals and aryloxy radicals containing 6 to 10 carbon atoms each and being unsubstituted or substituted by one or more identical

.../2

or different atoms or radicals chosen from halogen atoms and alkyl, alkoxy, aryloxy or alkoxycarbonyl radicals, and n is 0 or 1, which comprises reacting concentrated sulphuric acid rapidly at a temperature of 150° to 250°C, with a glycol of formula:



in which R_1, R_2, R_3, R_4, R_5, R_6 and n are as defined above, and recovering the cyclic sulphate obtained.

618092

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

NAME & ADDRESS
OF APPLICANT:

Rhone-Poulenc Sante
20 Avenue Raymond Aron
Antony F-92160
France

NAME(S) OF INVENTOR(S):

Viviane MASSONEAU
Michel MULHAUSER

ADDRESS FOR SERVICE:

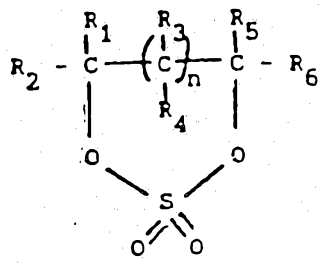
DAVIES & COLLISON
Patent Attorneys
1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

Process for the preparation of cyclic sulphates

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

The present invention relates to the preparation of cyclic sulphates of general formula:



(I)

in which the substituents R_1, R_2, R_3, R_4, R_5 and R_6, which are identical or different, denote a hydrogen or halogen atom or an alkyl, aryl, alkoxy, aryloxy or alkoxycarbonyl radical and n is equal to 0 or 1.

In what precedes and what follows it is understood:

- that the alkyl radicals and the alkyl moieties of the alkoxy or alkoxycarbonyl radicals contain 1 to 4 carbon atoms each and may be optionally substituted by one or more identical or different atoms or radicals chosen from halogen atoms and alkoxy, aryloxy or alkoxycarbonyl radicals,
- that the aryl radicals and the aryl moieties of the aryloxy radicals contain 6 to 10 carbon atoms each and may be optionally substituted by one or more identical or different atoms or radicals chosen from halogen atoms and alkyl, alkoxy, aryloxy or alkoxycarbonyl radicals.

More particularly, the present invention relates to the preparation of cyclic sulphates of general formula (I)

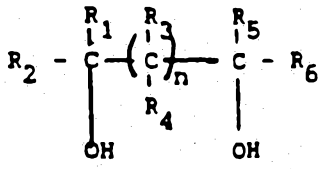
in which n is equal to 0 or 1 and the symbols R_1, R_2, R_3, R_4, R_5 and R_6, which are identical or different, denote a hydrogen atom or an alkyl radical.

The sulphates of general formula (I) are intermediates which can be employed in organic chemistry, in particular to perform hydroxyethylation reactions.

According to German Patent DE 1,049,870 it is known to prepare ethylene sulphate by heating a mixture of ethylene glycol, sulphuric acid and an excess of thionyl chloride under reflux for 50 hours.

It is also known, according to J. Lichtenberger and R. Lichtenberger, Bull. Soc. Chim. (France), 1002 (1948) to prepare cyclic sulphates of diols by reaction of an oleum with a chloroform solution of the diol, using at least two moles of free SO_3 per mole of diol, the oleum having a concentration of 47% of SO_3. However, while this method is suitable for primary-secondary diols, it does not work in the case of ethylene glycol.

It has now been found, and this is what forms the subject matter of the present invention, that cyclic sulphates of general formula (I) may be obtained by a simple and inexpensive process which consists in rapidly reacting, at a temperature of between 150 and 250°C, concentrated sulphuric acid with a glycol of general formula:



(II)

in which R_1, R_2, R_3, R_4, R_5, R_6 and n are defined as above.

In the new process the glycol of formula II and the concentrated sulphuric acid in the liquid or, preferably, the vapour phase are kept in contact at the reaction temperature in the range 150° to 250°C for no more than one hour, preferably from less than 1 second to 30 minutes.

The cyclic sulphate of general formula (I) is trapped by cooling (ie. by condensation from the vapour phase) or by dissolving it in a suitable solvent.

A substantially equimolar mixture of glycol of general formula (II) and of concentrated sulphuric acid is generally employed.

The process is preferably carried out under a reduced pressure, generally in the region of 1 mm Hg (0.13 kPa), and in the vapour phase.

For example, the process may be carried out by rapidly passing the mixture of concentrated sulphuric acid and of glycol of general formula (II) through a tubular reactor heated to a temperature of between 150 and 250°C and kept under reduced pressure.

It may be advantageous to convey the mixture of reactants using an inert carrier gas.

The following Example shows how the invention may be put into practice.

EXAMPLE

Ethylene glycol (6.2 g, 0.1 mole) and 97% sulphuric acid (9.8 g, 0.097 mole) are mixed.

The mixture (2.5 g) is introduced with a syringe into the reactor shown in the accompanying Figure 1. The reactor is heated to 200°C by means of a heating tape. The apparatus is placed under a reduced pressure of 1 mm Hg (0.13 kPa). The residence time of the ethylene glycol - sulphuric acid mixture in the heated part of the reactor is 10 minutes.

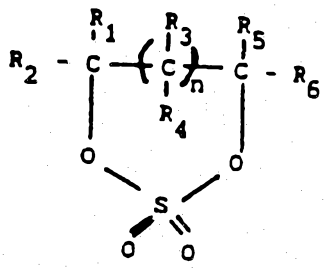
The ethylene sulphate formed is collected in the Vigreux column placed in a jacket containing solid CO_2. When the reaction is finished, the Vigreux column is rinsed with dichloromethane. After the solution obtained has been separated and the dichloromethane evaporated, ethylene sulphate (0.85 g) is obtained in the form of white crystals. The yield is 45% based on the sulphuric acid employed.

In Figure 1:

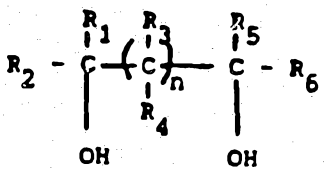
- (1) shows the orifice for introducing the reactants;
- (2) shows a reactant flow tube;
- (3) shows a heating tape;
- (4) shows the receiver for collecting the ethylene sulphate after rinsing of the Vigreux column;
- (5) shows a Vigreux column;
- (6) shows a cooling jacket; and
- (7) shows the vacuum adaptor.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS.

1. A process for the preparation of a cyclic sulphate of formula:



in which R_1, R_2, R_3, R_4, R_5 and R_6, which are identical or different, each denote a hydrogen or halogen atom or an alkyl, aryl, alkoxy, aryloxy or alkoxycarbonyl radical and n is 0 or 1, the aforesaid alkyl radicals and the alkyl moieties of the alkoxy and alkoxycarbonyl radicals containing 1 to 4 carbon atoms each and being unsubstituted or substituted by one or more identical or different atoms or radicals chosen from halogen atoms and alkoxy, aryloxy or alkoxycarbonyl radicals, and the said aryl radicals and aryloxy radicals containing 6 to 10 carbon atoms each and being unsubstituted or substituted by one or more identical or different atoms or radicals chosen from halogen atoms and alkyl, alkoxy, aryloxy or alkoxycarbonyl radicals, and n is 0 or 1, which comprises reacting concentrated sulphuric acid rapidly at a temperature of 150° to 250°C, with a glycol of formula:



in which R_1, R_2, R_3, R_4, R_5, R_6 and n are as defined above, and recovering the cyclic sulphate obtained.

2. A process according to claim 1 in which R_1, R_2, R_3, R_4, R_5 and R_6, which are identical or different, each denote a hydrogen atom or an alkyl radical and n is 0 or 1.

3. Process according to claim 1 or 2, wherein a substantially equimolar mixture of the glycol and of concentrated sulphuric acid is used.

4. Process according to any one of claims 1 to 3, wherein the reaction is carried out under reduced pressure.

5. Process according to claim 4, wherein the reaction is carried out at about 1 mm Hg or 0.13 kPa.

6. Process according to any one of claims 1 to 5 wherein the reaction is effected in the vapour phase and the mixture of the glycol and sulphuric acid is diluted with an inert gas.

7. Process according to claim 1 substantially as described in the Example.

8. Cyclic sulphates when produced by the process of any of claims 1 to 7.

9. The steps, features, compositions and compounds disclosed herein or referred to or indicated in the specification and/or claims of this application, individually or collectively, and any and all combinations of any two or more of said steps or features.

DATED this FIFTEENTH day of MAY 1989

Rhone-Poulenc Sante

by DAVIES & COLLISON
Patent Attorneys for the applicant(s)

AUSTRALIAN PATENT OFFICE

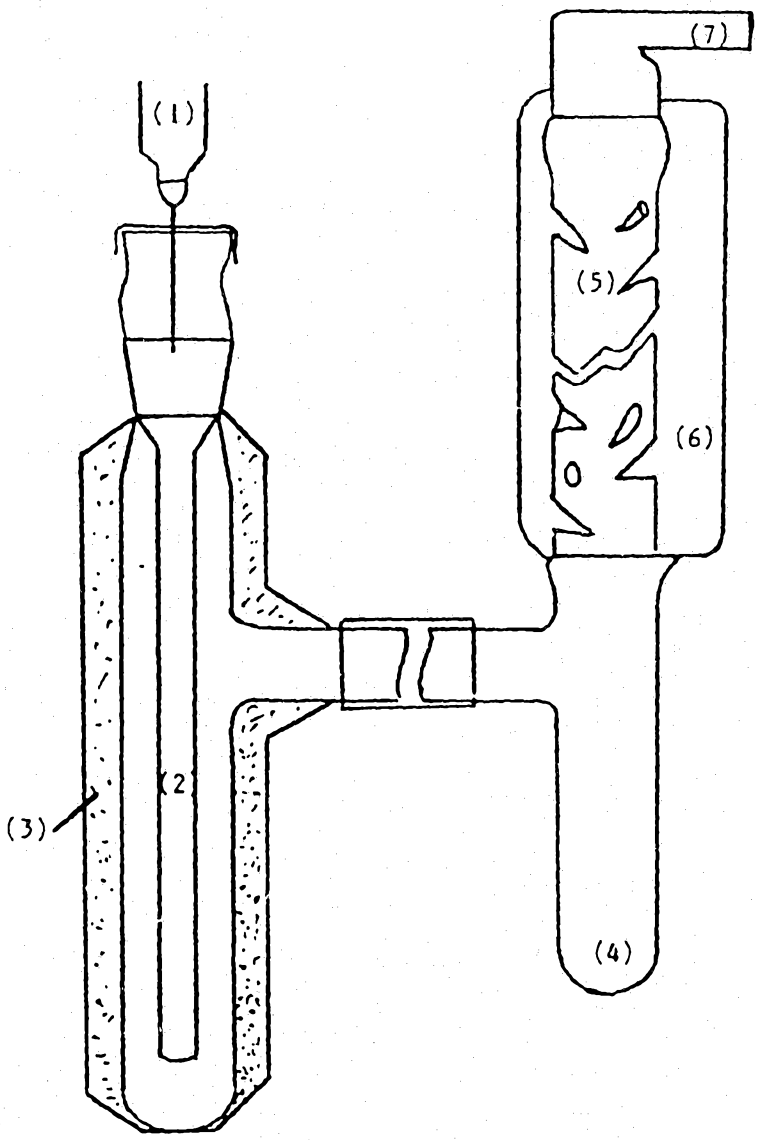


FIGURE 1