

628378

COMMONWEALTH of AUSTRALIA  
Patents Act 1952

APPLICATION FOR A STANDARD PATENT

I/We

Sandoz Ltd.

of

Lichtstrasse 35, CH-4002 Basle, Switzerland

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

"Polysulphide Sealing Compositions".

which is described in the accompanying complete specification.

Details of basic application(s):-

Number

Convention Country

Date

P 38 30 495.3

Federal Republic of Germany

8 September 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 SIXTH day of SEPTEMBER 1989

To: THE COMMISSIONER OF PATENTS

*Keith Collison*

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

Davies & Collison, Melbourne



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AUSTRALIA

*Patents Act 1990*

NOTICE OF ENTITLEMENT

We, **Sandoz Ltd.** the applicant in respect of Application No. 41064/89, state the following:-

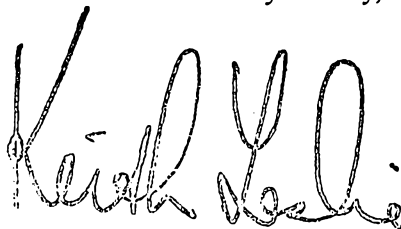
Karoly Dischö is the inventor in respect of the invention.

The Nominated person(s) is/are entitled to the grant of the patent because the Nominated person(s) derives title to the invention from the inventor(s).

The Nominated person(s) is/are entitled to claim priority from the basic application(s) listed on the patent request because the Nominated person has the consent of the applicant(s) in respect of the basic application(s) to make a convention application based on the basic application(s).

The basic application(s) is/are the first application(s) made in a Convention country in respect of the invention.

Dated this 10th day of July, 1992



(A member of the firm of DAVIES COLLISON CAVE for  
and on behalf of the applicant)

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**(12) PATENT ABRIDGMENT      (11) Document No. AU-B-41064/89**  
**(19) AUSTRALIAN PATENT OFFICE      (10) Acceptance No. 628378**

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- (54) Title  
**SULFIDE GROUP-CONTAINING POLYMER COMPOSITION**
- (51)<sup>4</sup> International Patent Classification(s)  
**C08L 081/02      C08K 005/09      C08L 071/00      C08L 075/04**  
**C08L 101/00      C09K 003/10      E04B 001/66**
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- (71) Applicant(s)  
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- (72) Inventor(s)  
**KAROLY DISCHO**
- (74) Attorney or Agent  
**DAVIES COLLISON CAVE , 1 Little Collins Street, MELBOURNE VIC 3000**
- (56) Prior Art Documents  
**EP 0060669**
- (57) Claim

1. A composition suitable for use in sealing comprising

i) a polymeric compound which is a bi- and/or trifunctional polymeric compound having sulphide groups, and is selected from

polyether compounds A<sub>1</sub>),  
hydrocarbon polymer compounds A<sub>2</sub>),  
polysulphide polythiol polymer compounds A<sub>3</sub>),  
polyalkylene sulphide polymer compounds A<sub>4</sub>) and  
polyurethane compounds A<sub>5</sub>), and  
mixtures of such compounds,

(hereinafter defined as component i); and

ii) a hydroxy aromatic carboxylic acid (hereinafter defined as component ii).

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18. A two pack sealing composition comprising a composition according to any one of the preceding claims and a hardening agent.

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COMMONWEALTH OF AUSTRALIA  
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COMPLETE SPECIFICATION

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COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

"Polysulphide Sealing Compositions".

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



# POLYSULPHIDE SEALING COMPOSITIONS

The invention relates to novel compositions containing a polysulphide suitable for use as a sealing compound, which compositions have improved storage stability and which can be used as crosslinkable sealing compounds in the building industry.

Liquid polysulphides (thioplasts) and comparable polymers have been known for a long time as raw materials for the so-called "elastic" sealing compounds. They crosslink by reaction with oxidation agents, causing the terminal mercaptan groups to be converted into disulphide bridges of the elastic polysulphide molecule. Crosslinking can also take place by means of auto-oxidation for example with the oxygen found in air. This however impairs the storage stability of the sealing compounds, since an ever-increasing elastic layer forms on the surface of the compound, which finally renders the product useless. It is also known that this cross-linking can be controlled by using retarding agents such as stearic acid, which imparts to the sealing compounds a certain, but still insufficient storage stability.

To alleviate this problem, there is provided a composition suitable for use in sealing comprising

- i) a polymeric compound which is a bi- and/or trifunctional polymeric compound having sulphide groups, and is selected from

polyether compounds  $A_1$ ),  
hydrocarbon polymer compounds  $A_2$ ),  
polysulphide polythiol polymer compounds  $A_3$ ),  
polyalkylene sulphide polymer compounds  $A_4$ ) and



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polyurethane compounds A<sub>5</sub>), and mixtures of such compounds,

(hereinafter defined as component i); and

ii) a hydroxy aromatic carboxylic acid (hereinafter defined as component ii).

Preferably component i) is present in an amount of 3 to 99.9 parts more preferably 15 to 50 parts, most preferably 30 to 40 parts (based on 100 parts by weight of composition).

These polymeric compounds have a molecular weight greater than 1000 and are defined in Ullmanns Encyklopädie der Technischen Chemie, 4th edition, volume 14 (1977) the contents of which are incorporated by reference.

The polymeric compounds of component i) which are commercially available are for example "Thiokol" LP (trade mark) (Thiokol Chem. Corp., Trenton/N.J., USA) and Thioplast G (VEB-Chemiewerk, Greiz-Dölau) products.

It would appear that the aromatic hydroxy carboxylic acid act as a retarding agent for antioxidative crosslinking and thereby provides satisfactory storage stability for component i), without adversely affecting the time for crosslinking after addition of the oxidation agents.

Preferably component ii) is a hydroxy benzoic acid.

Component ii) is preferably present in an amount of 0.1 to 10 parts, more preferably 0.5 to 5 parts based on 100 parts of component i).

Preferably, component ii) may additionally include an aromatic carboxylic acid, more preferably benzoic acid. In such a case the amount of aromatic carboxylic acid present is preferably 0.1 to 9.9



parts, more preferably 0.5 to 5 parts based on 100 parts of component i) preferably in a ratio of 2:1 to 1:2 of the hydroxy aromatic carboxylic acid to aromatic carboxylic acid. Preferably the ratio of hydroxy aromatic carboxylic acid to aromatic carboxylic acid is about 1:1.

Compositions according to the invention may also contain one or more of the further components (herein defined as component iii) selected from the following:

softeners (such as chloroparaffin and benzylbutyl phthalate), active and inactive fillers (carbon black, pyrogenic silicic acids and calcium carbonate),

pigments (titanium dioxide and lampblack) and

other known additives as defined in Ullmann's Encyklopädie der Technischen Chemie, 4th edition, volume 14 (1977), page 261 to 265, the contents of which are incorporated herein by reference.

Preferably in a composition according to the invention, there is 45 to 70% of component iii).

Compositions according to the invention are normally free of any solvent, such as water and/or organic solvents.

During the production of the compositions according to the invention, component ii) (optionally with a softener in the form of a solution), is added to the liquid polymer prior to adding any other products of component iii), and the remaining components are mixed with the "stabilised" polymer in the conventional order at an elevated temperature, preferably at temperatures of 50-60°C.

In a preferred embodiment, hydroxybenzoic acid is mixed with a softener, e.g. benzylbutyl phthalate, to form a solution containing preferably 1-10% hydroxybenzoic acid. The solution is incorporated with the liquid polymer before the solid components.

The compositions according to the invention may be used as one component in two pack sealing compositions, adhesive components, coating masses, fillers and joint sealing compounds in the building

industry. For this purpose, shortly before use, they are mixed in known manner with hardening agents, i.e. so-called 2K-oxidation agents, such as lead dioxide or manganese dioxide pastes, and cross-linking occurs within 2 to 3 days. Prior to adding these hardening agents, however, the compositions according to the invention can remain stable in storage for as long as several months at room temperature. This can be tested by artificially exposing the composition to a temperature of 70°C and observing how long it takes for an undesirable skin formation to occur (which is induced after a few days). This has a correlation with the storing stability observed in practice.

Further according to the invention there is provided a two pack sealing composition comprising a composition according to the invention described above and a hardening agent (hereinafter defined as the hardener).

Preferred hardening agents used with the compositions of the invention are selected from lead dioxide paste, a manganese dioxide paste, zinc oxide and inorganic or organic peroxides.

These hardeners can also be used in the form of hardener compositions comprising the hardener and one or more compounds selected from fillers, softeners, other polymers such as epoxy resins and catalysts to speed up hardening. Such a preferred composition comprises

- i) zinc oxide, lead dioxide or manganese dioxide;
- ii) optionally an amino containing compound and
- iii) a disulphide (e.g tetramethylthiuram disulphide) (as catalysts).

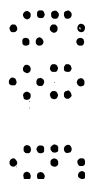
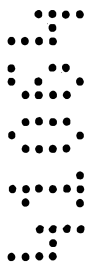
A preferred hardener composition comprises (based on 100 parts of hardener composition)

- i) 2 to 50 parts of zinc oxide, lead dioxide or manganese dioxide;
- ii) 10 to 60 parts of softeners and fillers (e.g. benzylbutyl

phthalate, chloro paraffin and silicic acid) and  
iii) 1 to 10 parts of a disulphide (e.g tetramethylthiuram  
disulphide).

Preferably 5 to 20 parts (more preferably 6 to 10 parts) of a  
hardener or hardener compositions defined above are mixed in use with  
100 parts of a composition according to the invention.

Based on 100 parts of component i) 1 to 60 parts of zinc oxide, 4 to 9  
parts of lead dioxide or 7 to 11 parts of manganese dioxide should be  
added in order to crosslinking to occur within 2-3 days.



The invention will now be illustrated by the following Examples in which all parts are by weight.

#### EXAMPLES 1 TO 10

Preparation of the composition is effected by mixing the components in the order given in a vacuum mixer. The 2-hydroxybenzoic acid is used as a solution in benzylbutyl phthalate only in Examples 5 to 10. Care must be taken that the mixing temperature as far as possible does not exceed 60°C. The compositions can be seen in Tables 1 and 2 below.

Table 1

| Examples                                                                                         | 1     | 2     | 3     | 4     |
|--------------------------------------------------------------------------------------------------|-------|-------|-------|-------|
| Polysulphide("Thiokol R" LP 32)                                                                  | 44    | 44    | 44    | -     |
| Polyetherpolyol with terminal mercapto groups (viscosity ca. 60,000 mPa.sec., SH content ca. 2%) | -     | -     | -     | 44    |
| 2-hydroxybenzoic acid                                                                            | 0.05  | 0.2   | 1.0   | 0.05  |
| calcium carbonate                                                                                | 24    | 24    | 24    | 24    |
| titanium dioxide                                                                                 | 20    | 20    | 20    | 20    |
| flowers of sulphur                                                                               | 0.05  | 0.05  | 0.05  | 0.05  |
| chloroparaffin                                                                                   | 11.90 | 11.75 | 10.95 | 11.90 |
|                                                                                                  | 100   | 100   | 100   | 100   |

Table 2

| Examples               | 5     | 6     | 7     | 8     | 9     | 10    |
|------------------------|-------|-------|-------|-------|-------|-------|
| Polysulphide           |       |       |       |       |       |       |
| ("Thiokol R" LP32)     | 30    | 30    | 30    | -     | 31    | 20    |
| Thiokol R LP3          |       |       |       |       | 3     |       |
| LP2                    |       |       |       |       |       | 10    |
| Polyether polyol (1)   | -     | -     | -     | 30    | -     | -     |
| 2-hydroxybenzoic acid  | 0.3   | 0.2   | 1.0   | 0.05  | 0.2   | 0.2   |
| benzylbutyl phthalate  | 14    | 14    | 14    | 14    | 15    | 14    |
| benzyl alcohol         | -     | -     | -     | -     | 2     | -     |
| benzoic acid           | 0.25  | -     | -     | -     | -     | -     |
| iron oxide black       | 6     | -     | -     | -     | -     | -     |
| calcium carbonate      | 45.45 | 22    | 22    | 22    | 46.8  | 23    |
| titanium dioxide       | -     | 20    | 20    | 20    | -     | 20    |
| lamp black             | -     | 1     | 1     | 1     | 2     | -     |
| pyrogenic silicic acid | -     | 1     | 1     | 1     | -     | 1     |
| flowers of sulphur     | -     | 0.05  | 0.05  | 0.05  | -     | 0.75  |
| chloroparaffin         | -     | 11.75 | 10.95 | 11.90 | -     | 11.75 |
|                        | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

1) is the same polyether polyol as in Table 1.

If in Examples 1-4, 1 part of lamp black is additionally added, grey coloured sealing compositions can be obtained (Examples 6-8) and if as in examples 5 and 9 titanium dioxide is missing, black sealing compositions are obtained.

In Examples 5 to 10, by adding benzylbutyl phthalate, the sealing composition becomes more supple, and by adding 1 part of pyrogenic silicic acid, somewhat lower tensile stress values are obtained, while the other properties remain unchanged (see Examples 6-8 and 10).

Application Example A

100 parts of the composition of Example 7 is mixed with 6 parts of a hardener composition comprising

49.0% manganese dioxide  
2.4% tetramethylthiuramdisulphide and  
48.6% benzylbutylphthalate

This produces a grey coloured sealant having good resistance to continuous stress which solidifies at 35°C within 3 hours and has a time for crosslinking of 1 day.

Application Example B

100 parts of the composition of Example 9 is mixed with 8 parts of a hardener composition comprising

40% lead dioxide  
3% tetramethylthiuramdisulphide and  
57% benzylbutylphthalate

A black coloured mass having an elongation at break point after crosslinking of 200%.

Application Example C

100 parts of the composition of Example 10 is mixed with 14 parts of a hardener composition comprising

38% zinc oxide  
2% N,N-diphenylguanidine  
6% tetramethylthiuram disulphide  
2% pyrogenic silicic acid and  
52% chloroparaffin

A white sealing mass results with good stability which takes 3 days to crosslink fully.

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The claims defining the invention are as follows:

1. A composition suitable for use in sealing comprising

- i) a polymeric compound which is a bi- and/or trifunctional polymeric compound having sulphide groups, and is selected from

polyether compounds  $A_1$ ),  
hydrocarbon polymer compounds  $A_2$ ),  
polysulphide polythiol polymer compounds  $A_3$ ),  
polyalkylene sulphide polymer compounds  $A_4$ ) and  
polyurethane compounds  $A_5$ ), and  
mixtures of such compounds,

(hereinafter defined as component i); and

- ii) a hydroxy aromatic carboxylic acid (hereinafter defined as component ii).

2. A composition according to Claim 1 in which component i) is a polysulphide.
3. A composition according to Claim 2 in which the polysulphide is a liquid polysulphide.
4. A composition according to any one of the preceding claims in which component i) is present in an amount of 3 to 99.9 parts (based on 100 parts of composition).
5. A composition according to any one of the preceding claims in which component ii) is a hydroxy benzoic acid.
6. A composition according to any one of the preceding claims in which component ii) is 2-hydroxy benzoic acid.
7. A composition according to any one of the preceding claims in



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which component ii) is present in an amount of 0.1 to 10 parts based on 100 parts by weight of component i).

8. A composition according to Claim 7 in which component ii) is present in an amount of 0.5 to 5 parts based on 100 parts by weight of component i).
9. A composition according to any one of the preceding claims in which component ii) may additionally include an aromatic carboxylic acid.
10. A composition according to Claim 9 in which the aromatic carboxylic acid is benzoic acid.
11. A composition according to Claim 9 or 10 in which the amount of aromatic carboxylic acid present is 0.1 to 9.9 parts based on 100 parts by weight of component i).
12. A composition according to Claim 11 in which the amount of aromatic carboxylic acid present is 0.5 to 5 parts based on 100 parts of component i).
13. A composition according to Claims 10 to 12 in which the hydroxy aromatic carboxylic acid and aromatic carboxylic acid are present in a weight ratio of 2:1 to 1:2 of the hydroxy aromatic carboxylic acid to aromatic carboxylic acid.
14. A composition according to Claim 13 in which the weight ratio of hydroxy aromatic carboxylic acid to aromatic carboxylic acid is about 1:1.
15. A composition according to any one of the preceding claims containing one or more of the further components (herein defined as component iii) selected from the following:

softeners,  
active and inactive fillers, and



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pigments.

16. A composition according to Claim 15 in which the proportion of component iii) present is 45 to 70% by weight.
17. A polysulphide containing composition substantially as herein defined with reference to any one of Examples 1 to 10.
18. A two pack sealing composition comprising a composition according to any one of the preceding claims and a hardening agent.
19. A two pack sealing composition according to Claim 18 in which the hardening agent is selected from lead dioxide paste, a manganese dioxide paste, zinc oxide and organic peroxides (hereinafter defined as the hardener).
20. A two pack sealing composition according to Claims 18 and 19 in which the amount of hardener is 5 to 20 parts used with 100 parts of a composition according to any one of Claims 1 to 17.
21. A two pack sealing composition according to any one of Claims 18 to 20 in which the amount of hardener used is 6 to 10 parts per 100 parts of composition.
22. A two pack sealing composition according to any one of Claims 18 to 21 in which the hardener is used in the form of a hardener composition comprising the hardener and one or more compounds selected from fillers, softeners and catalysts to speed up hardening.
23. A two pack sealing composition according to Claim 22 in which the hardener composition comprises
  - i) zinc oxide, lead dioxide or manganese dioxide;
  - ii) optionally an amino containing compound (as catalyst); and
  - iii) a disulphide.



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24. A two pack sealing composition according to Claim 23 in which the hardener composition comprises (based on 100 parts of hardener composition)

- i) 2 to 50 parts of zinc oxide, lead dioxide or manganese dioxide;
- ii) 10 to 60 parts of softeners and solvents; and
- iii) 1 to 10 parts of a disulphide

25. A two pack sealing composition substantially as herein described with reference to any one of Application Examples A to C.

Dated this 10th day of July , 1992

SANDOZ LTD.  
by its patent attorneys  
Davies Collison Cave

