

CONTROLLED CURING OF POLYMERS

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 containing at least one sulphide group, [preferably a polysulphide, more preferably a liquid polysulphide] (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).

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Preferred polymeric compounds which may be used as component i) are bi- and/or trifunctional polymeric compounds having sulphide groups, especially

polyether compounds A₁),
hydrocarbon polymer compounds A₂),
polysulphide polythiol polymer compounds A₃),
polyalkylene sulphide polymer compounds A₄) or
polyurethane compounds A₅) or
mixtures of such compounds.

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-Dörlau) 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 10

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

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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 crosslinking occurs within 2 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 at 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 in one pack a composition according to the invention described above and in the other pack 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 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 hardeners 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 catalyst).

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

- i) 2 to 50 parts of zinc oxide, lead dioxide or manganese dioxide;
- ii) 10 to 50 parts of softeners and solvents (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.

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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	22	22	22	22
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
	98	98	98	98

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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	0.05	0.2	1.0	0.05	0.02	0.02
benzylbutyl phthalate	14	14	14	14	15	14
calcium carbonate	22	22	22	22	46.8	23
titanium dioxide	20	20	20	20	-	20
lamp black	1	1	1	1	2	-
pyrogenic silicic acid	1	1	1	1	-	1
flowers of sulphur	0.05	0.05	0.05	0.05	-	0.75
chloroparaffin	11.90	11.75	10.95	11.90	-	11.75
iron oxide black	6	-	-	-	-	-
benzyl alcohol	-	-	-	-	2	-
benzoic acid	0.25	-	-	-	-	-
	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.



CLAIMS

1. A composition suitable for use in sealing comprising
 - i) a polymeric compound containing at least one sulphide group, (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 by weight of composition).
5. A composition according to Claim 1 or 4 in which the polymeric compound which may be used as component i) is a bi- and/or trifunctional polymeric compound having sulphide groups, and is selected from
 - polyether compounds A₁),
 - hydrocarbon polymer compounds A₂),
 - polysulphide polythiol polymer compounds A₃),
 - polyalkylene sulphide polymer compounds A₄) and
 - polyurethane compounds A₅) and
 - mixtures of such compounds.
6. A composition according to any one of the preceding claims in which component ii) is a hydroxy benzoic acid.
7. A composition according to any one of the preceding claims in which component ii) is 2-hydroxy benzoic acid.



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8. A composition according to any one of the preceding claims in which component ii) is present in an amount of 0.1 to 10 parts based on 100 parts by weight of component i).
9. A composition according to Claim 8 in which component ii) is present in an amount of 0.5 to 5 parts based on 100 parts by weight of component i).
10. A composition according to any one of the preceding claims in which component ii) may include an aromatic carboxylic acid additional to the hydroxy aromatic carboxylic acid.
11. A composition according to Claim 10 in which the aromatic carboxylic acid is benzoic acid.
12. A composition according to Claim 10 or 11 in which the amount of aromatic carboxylic acid present is 0.1 to 10 parts based on 100 parts by weight of component i).
13. A composition according to Claim 12 in which the amount of aromatic carboxylic acid present is 0.5 to 5 parts based on 100 parts by weight of component i).
14. A composition according to Claims 11 to 13 in which the hydroxy aromatic carboxylic acid and additional aromatic carboxylic acid are present in a weight ratio of 2:1 to 1:2.
15. A composition according to Claim 14 in which the weight ratio of hydroxy aromatic carboxylic acid to additional aromatic carboxylic acid is about 1:1.
16. 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:



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softeners,
active and inactive fillers, and
pigments.

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



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iii) a disulphide (as catalyst).

25. A two pack sealing composition according to Claim 24 in which the hardener composition comprises (based on 100 parts by weight 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

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