

The invention relates on the one hand to the reactive composition for the production of a synthetic resin body which is used for anchoring fixing elements in a fixing base by the use of destructible multi-chamber cartridges. In particular the invention is directed to a given
5 combination of components of the reactive composition for the production of a synthetic resin body, a destructible multi-chamber cartridge for anchoring fixing elements in a fixing base, and an anchoring method in which the multi-chamber cartridge contains the special reactive composition.

10

It has long been known to use curing synthetic resins for securely fixing anchor rods and the like in slippery rock, brickwork, concrete and the like. In that situation the starting components of the synthetic resin and the synthetic resin hardener are brought separately from each
15 other to the fixing location and there mixed by the operation of driving in the fixing element. The formation of the hardened synthetic resin body which glues the fixing element to the fixing base is only initiated when the fixing element is in its final position.

20

That procedure owes its spread which in the meantime has become wide inter alia to the use of destructible cartridges which permit resin components and synthetic resin hardeners to be conveniently introduced into bore holes for anchor rods while in addition facilitating storage, transportation and metering of the reactive starting materials of the
25 synthetic resin body.

Cartridges which contain reactive compositions for the production of hardened synthetic resin bodies have already been described in DE-A-12 05 038 in connection with a process for fixing anchor rods without a
30 spreading head in fitting anchors in mining areas. They involve glass or bakelite cartridges comprising a filling of hardenable polyester or epoxy resin and the same or a larger amount by weight of quartz sand or dust, and a capsule which is introduced into the filling of the cartridge and which contains the hardener. That specification provides that organic
35 peroxides are used in relation to polyesters. If pre-accelerated epoxy resins are used, then use is made of an amine hardener. Although cartridges with reactive compositions of that kind have been used for a number of years in the fixing art, they do however suffer from serious disadvantages. Those disadvantages lie in the slow curing of pre-
40 accelerated epoxy resins with amine hardeners so that, when there is a requirement for the fixing element to be able to carry a loading quickly, the glass cartridge and the anchor rod must be pre-heated to temperatures above 150°C. The peroxide-hardened polyester resins suffer from the disadvantage that they are not sufficiently resistant to chemicals and in
45 particular are not alkali-resistant. Particularly when dealing with a basic fixing base, that results in the long term in a reduction in the level of mechanical properties of the synthetic material body. In addition, hardened polyester resins of that kind also have a relatively high level of absorption of water, which can give rise to corrosion
50 problems in connection with metal fixing elements.

In order to eliminate the disadvantages of known materials of that kind, EP-A-O 150 555 proposed two-chamber cartridges in which a fine-grain natural or synthetic mineral filler substance is disposed together with a vinyl ester epoxy resin on an acrylate or methacrylate base in the inner or outer chamber of a two-chamber cartridge which is made up of two glass cylinders fitted one within the other, while the hardener, an organic peroxide, is disposed in the respective other chamber. The particularity of the cartridges in accordance with EP-A-O 150 555 is that a reactive vinyl monomer is mixed with the resin component.

The synthetic resin materials in accordance with EP-A-O 150 555 represent a significant development in comparison with previously known resin compositions insofar as on the one hand they cure more quickly than the epoxy resins used hitherto while on the other hand they are superior to the polyester resins used hitherto, in respect of resistance to alkalis. Nonetheless the synthetic material bodies which in accordance with the disclosure of EP-A-O 150 555, are obtained after shattering of the glass cartridges and curing of the components of the reactive composition, also suffer from serious disadvantages:

On the one hand synthetic resin bodies of that kind do not represent a sufficiently effective diffusion barrier in relation to reactive compounds such as hydrochloric acid or diffusing water vapour. In the final effect, that relatively high level of transmissibility in respect of low-molecular substances results in a reduction in the resistance to corrosion of the metal fixing element. Another serious disadvantage of the anchorages which are obtained by means of the synthetic resin bodies in accordance with the provisions of EP-A-O 150 555 lies in their mechanical characteristics. Under a continuous loading, the synthetic resin bodies produced in that way have a tendency to become soft. The resulting creep behaviour on the part of the resin matrix means that under a continuous loading, due to the danger of slippage of the fixing element with synthetic resin material of that kind, it is not possible to guarantee a secure anchorage effect over prolonged periods of time. Accordingly that type of resin is not suitable for many areas of use in the building industry, in which the fixing element must securely withstand a tensile loading which goes on over decades.

That disadvantage is made worse by virtue of the fact that the curing rate which is satisfactory to a certain extent and which provides that the fixing element can be subjected to a loading after a relatively short period of time is achieved by means of a high percentage of hardener component in the resin composition. The high percentage of organic peroxide, as disclosed in EP-A-O 150 555, admittedly provides for more rapid curing of the synthetic resin mixture, on the one hand, but on the other hand it has the undesirable side effect of also promoting rapid ageing of the synthetic resin body. The chemical changes which in the course of time reduce the adhesion capability of the resin with respect to the surrounding fixing base and the fixing element and which adversely

affect the internal structure and thus the strength of the synthetic resin material itself (embrittlement and a tendency to become friable) involve a further instability factor which makes long-term use thereof problematical.

5

Another disadvantage arises from the point that, in spite of a comparatively high curing speed at normal temperatures (25°C), it is still necessary to reckon on a curing time of several days and even elevated temperatures (35°C) require curing times in the region of hours, before the fixing element can be subjected to load. For many practical uses in which cost-intensive waiting times are caused by virtue of the fact that an anchored fixing element still cannot be subjected to a loading, the application of the teaching of EP-A-O 150 555 therefore gives rise to problems.

15

Another negative aspect of the state of the art is the unsatisfactory storage capability of the synthetic resin components in the cartridges, in particular at elevated temperature.

20

The problem of the present invention is to provide a reactive composition, in particular for use in multi-chamber cartridges, for the production of a synthetic resin body which provides for the anchoring of fixing elements in a fixing base, and is distinguished in that it provides for anchorages which can be subjected to a high loading after a short curing time and which remain stable without change under a continuous mechanical loading and exhibit a high level of resistance to acid and alkali, which forms an effective diffusion barrier in relation to low-molecular compounds and which have an equally high level of adhesion capability in relation to metals and natural and artificial mineral materials and which if necessary, without a reduction in the properties which are essential in a practical context, can be so designed as to enjoy a storage capability at elevated temperatures.

25

That problem is solved by the reactive composition for the production of synthetic resin bodies, in particular for use in destructible multi-chamber cartridges for anchoring of fixing elements in a fixing base, wherein the reactive composition includes a) a pre-accelerated resin component which contains the ester of an epoxy resin with acrylic and/or methacrylic acid and in addition one or more ethylenically unsaturated monomer or monomers as well as accelerators, polymerisation inhibitors and optionally other conventional additives,

35

b) a hardener component comprising an organic peroxide, and

45

c) a filler component,

which is characterised in that the reactive composition is constituted using

18 to 25 parts by weight of the pre-accelerated resin component,

0.4 to 1.2 parts by weight of the hardener component, and
40 to 55 parts by weight of the filler component,
and the pre-accelerated resin component contains as constituents

5

A) 3 to 60 parts by weight of vinyl ester epoxy resin,

B) 28 to 45 parts by weight of one or more ethylenically
unsaturated monomeric compounds, and

10

C) 63 to 3 parts by weight of an unsaturated polyester, and

D) 10 to 0.1 parts by weight of epoxy resin.

15

The invention also includes a destructible multi-chamber cartridge
for the in-situ production of synthetic resin bodies for the fixing of
anchoring elements in bore holes, wherein the cartridge contains the
reactive composition according to the invention and wherein the organic
peroxide hardener and the pre-accelerated resin component are disposed
separately from each other in different chambers.

20

The destructible multi-chamber cartridge according to the
invention is used in methods for anchoring a fixing element in a fixing
base by introducing a destructible multi-chamber cartridge which contains
the components of a hardenable adhesive and is introduced into a bore hole
in the fixing base, wherein by the fixing element being driven in the
cartridge is destroyed and the synthetic resin components are mixed,
whereupon the synthetic resin hardens.

25

The subsidiary claims set forth preferred embodiments of the
invention.

30

It was surprisingly found that the combination of components (A),
(B), (C) and possibly (D) provides the combination of properties for
solving the problem of the invention.

35

In that connection the addition of the epoxy resin (D) - epoxy
resins of type bisphenol A are preferably used - results in a considerably
increased storage capability of the synthetic resin component of the
reactive composition at elevated temperature (long-term storage capability
at temperatures around 50°C).

40

In a totally unexpected manner, in spite of the highly different
reactivity of the constituents (A) and (C) of the pre-accelerated resin
component, a homogenous, non-cloudy product is obtained. Another
surprising aspect is that there is no formation of gas bubbles during
hardening of the synthetic resin material from the reactive composition
according to the invention. In the final effect, that guarantees a

45

unitary synthetic resin body. The absence of non-homogeneity phenomena in the synthetic resin itself already eliminates a source of possible failure of the adhesive anchorage.

5 Without seeking to derive a theory therefrom, it is pointed out that with the novel reaction product from the reactive composition according to the invention with (A), (B), (C) and possibly (D) in the resin component, there is possibly a higher degree of cross-linking of the reaction product. The considerably higher level of resistance to
10 chemicals, in comparison with resins of the state of the art, can be afforded by better shielding of the ester groups, which occurs as a result.

Such a structure may also offer a plausible explanation for the
15 considerably improved resistance of the synthetic resin bodies made from the reactive composition according to the invention, in relation to diffusing media. In particular it must be emphasised that with the reactive composition according to the invention, there is a very high curing speed, in spite of the comparatively very small amount of peroxide
20 hardener. Reactive compositions which contain in the vinyl ester epoxy resin an epichlorhydrinepoxy resin of type bisphenol A are preferred in terms of the balance in respect of their reactivity, their miscibility under the conditions of rotational insertion of the anchor rods to be fixed, and the continuous load-carrying capacity which can be achieved in
25 respect of the resulting resin body. In regard to handlability and reactivity, it is preferred that generally the vinyl ester epoxy resin (A) has a mean molecular mass of 450 to 1200 Daltons, an ester value of 80 to 150 mg KOH/g of resin and, if it occurs in the form of a solution of 55 to 70% by weight (A) in the monomer used, a viscosity of 400 to 1000 mPas at
30 23°C.

Styrene and/or methyl methacrylate are particularly suitable as the ethylenically unsaturated monomer (B) by virtue of its satisfactory reactivity and the cost advantages which are linked to ease of
35 accessibility.

In regard to their chemical nature, in particular unsaturated polyesters on the basis of o-phthalic acid and/or m-phthalic acid or isophthalic acid with ethylene glycol and/or propylene glycol and/or
40 tricyclodecanedimethanol and/or neopentyl glycol are suitable as the polyester resins (C). In regard to reactivity and handlability (flow characteristics and miscibility), it is found to be preferable to use polyester resins (C) whose ester value is in the range of 180 to 320 mg KOH/g of resin and which, if they are in the form of a solution of 50 to
45 70% (C) of monomer used, have a viscosity of 800 to 6000 mPa s at 23°C. Particularly suitable as the epoxy resin component (D) are those whose epoxy equivalent weight is in the range of 160 to 200 g/equivalent and which have a viscosity of 2500 to 4000 mPas at 23°C.

The reactive composition according to the invention is preferably used in a multi-chamber cartridge which contains the hardener and the pre-accelerated resin component in different chambers. In that arrangement the filler may be disposed with the pre-accelerated synthetic resin in one
 5 chamber. That arrangement presents itself if the cartridge is in the form of a two-chamber cartridge, as is conventional practice in the state of the art.

Surprisingly, in relation to strength and durability of the
 10 anchorage for the fixing element, particularly good results can be achieved if, when the multi-chamber cartridge comprises glass, a weight ratio of 20 to 35 parts by weight of cartridge glass with 18 to 25 parts by weight of the pre-accelerated resin component of the reactive composition according to the invention, 0.4 to 1.2 parts by weight of
 15 peroxide hardener and 40 to 55 parts by weight of the filler component is observed.

In that connection the filler component preferably comprises fine-grain quartz, magnesia clinker, marble dust or the like.

20 In accordance with the invention, for the purposes of anchoring a fixing element in a fixing base, the best procedure is such that a destructible multi-chamber cartridge which contains the reactive composition according to the invention is introduced in per se known
 25 manner into a bore hole in the fixing base. Thereupon, by the fixing element being driven in, the cartridge is destroyed and the hardener which was previously separated from the pre-accelerated synthetic resin component is mixed with the material to be hardened and thus the hardening reaction is initiated in situ.

30 The following examples illustrate the way in which the present invention is carried into effect and clearly show the properties of the combination according to the invention, which are superior over the state of the art.

35 Comparative example:

Composition with vinyl ester epoxy resin

40	Vinyl ester epoxy resin	60.00 g
	Monostyrene	39.85 g
	Dimethyl-p-toluidine	0.15 g
		100.00 g

45 Ester value (EV) = 60 mg KOH/g of resin
 Viscosity at 23°C = 600 mPa s
 Long-term resistance, stored at 50°C = 2 to 3 months.

That long-term resistance is inadequate.

Example 1:

	Vinyl ester epoxy resin	47.85 g
	Unsaturated neopentyl glycol-m-phthalic acid polyester	12.00 g
5	Dimethyl-p-toluidine	0.15 g
	Monostyrene	<u>40.00 g</u>
		100.00 g

- 10 EV = 107 mg KOH/g of resin
 Viscosity at 23°C = 680 mPa s
 Long-term resistance, stored at 50°C = at least 6 months

Example 2:

15	Vinyl ester epoxy resin	31.00 g
	Unsaturated tricyclodecanedimethanol-o,m-phthalic acid polyester	30.85 g
	Dimethyl-p-toluidine	0.15 g
	Monostyrene	<u>38.00 g</u>
20		100.00 g

- EV = 150
 Viscosity at 23°C = 1500 mPa s
 25 Long-term resistance, stored at 50°C = at least 6 months

Example 3:

	Vinyl ester epoxy resin	46.40 g
30	Unsaturated tricyclodecanedimethanol polyester	11.60 g
	Dimethyl-p-toluidine	0.15 g
	Monostyrene	<u>41.85 g</u>
		100.00 g

- 35 EV = 93; viscosity at 23°C = 834 mPa s
 Long-term resistance, stored at 50°C = at least 6 months

Example 4:

40	Vinyl ester epoxy resin	40.00 g
	Unsaturated tricyclodecanedimethanol polyester	20.00 g
	Dimethyl-p-toluidine	0.15 g
	Monostyrene	17.85 g
45	Methyl methacrylate	12.00 g
	Epoxy resin with an epoxy equivalent of 200	<u>10.00 g</u>
		100.00 g

- 50 Viscosity at 23°C = 1250 mPa s
 Long-term resistance, stored at 50°C = at least 10 months

Example 5:

	Vinyl ester epoxy resin, pre-accelerated	3.00 g
	Unsaturated tricyclodecanedimethanol polyester	59.00 g
5	Monostyrene	<u>38.00 g</u>
		100.00 g

EV = 220 KOH/g resin

10 Viscosity at 23°C = 2800 mPa s

Long-term resistance, stored at 50°C = at least 6 months

Example 6:

15	Vinyl ester epoxy resin, pre-accelerated	60.00 g
	Unsaturated isophthalic acid neopentyl glycol polyester	8.00 g
	Monostyrene	31.00 g
	Epoxy resin with an epoxy equivalent of 200	<u>1.00 g</u>
20		100.00 g

EV = 84 KOH/g resin

Viscosity at 23°C = 550 mPa s

Long-term resistance, stored at 50°C = at least 10 months

25

Example 7:

	Vinyl ester epoxy resin, pre-accelerated	6.00 g
	Unsaturated tricyclodecanedimethanol polyester	63.00 g
30	Monostyrene	28.00 g
	Epoxy resin with an epoxy equivalent of 180	<u>3.00 g</u>
		100.00 g

35 EV = 152 KOH/g of resin, viscosity at 23°C = 4200 mPa s
 Long-term resistance, stored at 50°C = at least 10 months

Example 8:

40	Vinyl ester epoxy resin, pre-accelerated	14.60 g
	Unsaturated tricyclodecanedimethanol polyester	40.00 g
	Monostyrene	45.00 g
	Epoxy resin with an epoxy equivalent of 180	<u>0.40 g</u>
45		100.00 g

EV = 186 KOH/g of resin; viscosity at 23°C = 2000 mPa s

Long-term resistance, stored at 50°C = at least 10 months

Example 9:

	Vinyl ester epoxy resin, pre-accelerated	49.10 g
	Unsaturated tricyclodecanedimethanol polyester	12.30 g
5	Monostyrene	38.50 g
	Epoxy resin with an epoxy equivalent of 200	<u>0.10 g</u>
		100.00 g

- 10 EV = 110 KOH/g of resin; viscosity at 23°C = 750 mPa s
Long-term resistance, stored at 50°C = at least 10 months

Example 10:

Cartridge of size M 12 (metric thread)

15	Amine pre-accelerated resin component of Example 1	4.30 g
	Quartz (grain size 1.2-1.8 mm)	8.20 g
	Dibenzoyl peroxide (20% in gypsum)	0.54 g
	Cartridge glass (outer and inner cartridge)	<u>5.40 g</u>
20		18.44 g

Anchor rod M 12 x 160, threaded rod quality 12.9

Hardening time: 0.5 h

Concrete: B 50 actual strength: 54.2 N/mm²

- 25 Mean extraction value X: $\frac{2}{KN}$ - 101.7

Composite strength: N/mm² - 20.7; failure: anchor rod fractureExample 11:

Cartridge of size M 12 (metric thread)

30	Amine pre-accelerated resin component of Example 2	3.60 g
	Quartz (grain size 0.5-1.8 mm)	8.00 g
	Dibenzoyl peroxide (50% in phthalate plasticiser)	0.24 g
	Cartridge glass (outer and inner cartridge)	<u>5.45 g</u>
35		17.29 g

Anchor rod M 12 x 160, 12.9

Hardening time: 0.5 h

Concrete: B 50 actual strength: 54.2 N/mm²

- 40 Mean extraction value X: $\frac{2}{KN}$ - 96.3

Composite strength: N/mm² - 19.6

Failure: Composite failure - anchor rod fracture

Example 12:

Cartridge of size M 12 (metric thread)

45	Amine pre-accelerated resin component of Example 3	4.00 g
	Quartz (grain size 1.2-1.8 mm)	8.80 g
	Dibenzoyl peroxide (50% in phthalate plasticiser)	0.26 g
	Cartridge glass (outer and inner cartridge)	<u>5.37 g</u>
50		18.43 g

Anchor rod M 12 x 160, 12.9

Hardening time: 0.5 h

Concrete: B 50 actual strength: 54.2 N/mm^2

Mean extraction value X: KN - 99.9

5 Composite strength: N/mm^2 - 20.4

Failure: composite failure due to anchor rod fracture

CLAIMS

1. A reactive composition for the production of synthetic resin bodies, in particular for use in destructible multi-chamber cartridges for anchoring of fixing elements in a fixing base, wherein the reactive composition includes

a) a pre-accelerated resin component which contains the ester of an epoxy resin with acrylic and/or methacrylic acid and in addition one or more ethylenically unsaturated monomer or monomers as well as accelerators, polymerisation inhibitors and optionally other conventional additives,

b) a hardener component comprising an organic peroxide, and

c) a filler component,

characterised in that the reactive composition is constituted using

18 to 25 parts by weight of the pre-accelerated resin component,

0.4 to 1.2 parts by weight of the hardener component, and

40 to 55 parts by weight of the filler component,

and the pre-accelerated resin component contains as constituents

A) 3 to 60 parts by weight of vinyl ester epoxy resin,

B) 28 to 45 parts by weight of one or more ethylenically unsaturated monomeric compounds,

C) 63 to 3 parts by weight of an unsaturated polyester, and

D) 10 to 0.1 parts by weight of epoxy resin.

2. A reactive composition according to claim 1 characterised in that the vinyl ester epoxy resin (A) is constituted on the basis of an epichlorhydrinepoxy resin with acrylic and/or methacrylic acid, wherein an epichlorhydrinepoxy resin of type bisphenol A is preferably used.

3. A reactive composition according to claims 1 and 2 characterised in that the ethylenically unsaturated monomer (B) is styrene and/or methylmethacrylate.



4. A reactive composition according to claims 1 to 3 characterised in that the unsaturated polyester resin (C) is constituted on the basis of o-phthalic acid and/or m-phthalic acid with ethylene glycol and/or propylene glycol and/or tricyclodecanedimethanol and/or neopentylglycol.

5. A reactive composition according to claims 1 to 4 characterised in that the epoxy resin (D) is constituted on the basis of epichlorhydrine and bisphenol A.

6. A reactive composition according to claims 1 to 5 characterised in that the vinyl ester epoxy resin (A) has a mean molecular mass of 450 to 1200 Daltons.

7. A reactive composition according to claims 1 to 6 characterised in that the vinyl ester epoxy resin (A) has an ester value of 80 to 150 mg KOH/g of resin.

8. A reactive composition according to claims 1 to 7 characterised in that the vinyl ester epoxy resin (A) in the form of a solution of 55 to 70% by weight (A) in the monomer used in relation to the total weight of the solution has a viscosity of 400 to 1000 mPa s at 23°C.

9. A reactive composition according to claims 1 to 8 characterised in that the unsaturated polyester resin (C) has an ester value of 180 to 320 mg KOH/g of resin.

10. A reactive composition according to claims 1 to 9 characterised in that the unsaturated polyester resin (C) in the form of a solution of 50 to 70% by weight (C) in the monomer used, in relation to the total weight of the solution, has a viscosity of 800 to 6000 mPa s at 23°C.



11. A reactive composition according to claims 1 to 10 characterised in that the epoxy resin (D) has an epoxy equivalent weight of 160 to 200 g/equivalent.

12. A reactive composition according to claims 1 to 11 characterised in that the epoxy resin (D) has at 23°C a viscosity of 2500 to 4000 mPa s.

13. A destructible multi-chamber cartridge for the in-situ production of synthetic resin bodies for the fixing of anchoring elements in bore holes, characterised in that it contains the reactive composition according to claims 1 to 12, wherein the organic peroxide hardener and the pre-accelerated resin component are disposed separately from each other in different chambers.

14. A destructible multi-chamber cartridge according to claim 13 characterised in that it is in the form of a two-chamber cartridge.

15. A destructible multi-chamber cartridge according to claims 13 and 14 characterised in that it comprises glass.

16. A destructible multi-chamber cartridge according to claim 15 characterised in that the weight ratio of

20 to 35 parts by weight of cartridge glass

18 to 25 parts by weight of the pre-accelerated resin component

0.4 to 1.2 parts by weight of peroxide hardener and

40 to 55 parts by weight of the filler component

is observed.

17. A destructible multi-chamber cartridge according to claim 16 characterised in that the filler component comprises fine-grain quartz, magnesia klinker or marble dust or the like.



18. A method of anchoring a fixing element in a fixing base by introducing a destructible multi-chamber cartridge which contains the components of a hardenable adhesive and is introduced into a bore hole in the fixing base, wherein by the fixing element being driven in the cartridge is destroyed and the synthetic resin components are mixed, whereupon the synthetic resin hardens, characterised in that a destructible multi-chamber cartridge according to claims 13 to 16 is used.



* C L H S *