

OVM/WP-8 April 1997

P.ATAK.01/BE

Traduction de la publication PCT

5

**PROCESS FOR PROTECTING SURFACES AGAINST CORROSIVE
MATERIALS AND RESIN BASE PRODUCTS THEREFOR**

Object of the invention

10 The present invention relates to a process for
protecting surfaces by treating them with a composition
giving them a good resistance against corrosive or aggressive
materials such as chemical agents under liquid, gaseous or
smoke form, particularly strong and weak acids, alcalis,
15 salts, etc.

Such a protection can be applied under a diluted
form in a primer or in a pasty state with no diluent or as
a binder in a mortar mixed with sand, on surfaces of
concrete, asbestos-cement, steel, etc.

20 The invention also relates to a resin composition
suitable for use to implement such a process.

Technological background

After their coating under a substantially liquid
form on the surface to be treated, the resulting protection
25 films set forming thereby a protection film.

For most of the known compositions, this setting,
which implies generally network phenomenons, leads to a
shrinkage causing an adherence defect to the substrate.
Different thermal expansion and shrinkage properties of the
30 protection film and the substrate also lead, in service, to
numerous cohesion difficulties which can even lead to a
delamination.



Numerous requirements are formulated by the users, including mechanical properties (compression, tension, abrasion resistances, etc.), thermal resistance, the dry material/solvent ratio, life time and, of course, also the quality/price ratio. Coating easiness, including in severe conditions of room temperature and relative humidity of the atmosphere, and risks and dangers during coating, must also be taken into account.

Aims of the invention

The present invention aims at providing a process and a composition suiting to those requirements and, particularly, improved means to protect efficiently against chemical reactants, particularly against chemical attacks, namely alkaline and mainly acid ones, external and internal surfaces, particularly concrete tanks or steel tanks and containers as used generally in the chemical industry. Other applications can of course also be envisaged, such as building protections.

Characteristic features of the present invention

The invention relates to a process of protecting surfaces against corrosive materials, which consists in using a composition comprising a polystyrene, so-called impact-polystyrene, in a solution in an appropriate solvent, preferably in styrene, which is mixed in quantity of 1 to 18 parts, preferably approximately 4 parts, in weight of a vinyl or unsaturated polyester resin for one part in weight of the polystyrene solution, in the presence of accelerators or catalysts.

The polystyrene solution in the solvent thereof is preferably in such a concentration that an appropriate (syrup-like) fluidity is obtained. Preferably the polystyrene/styrene ratio is approximately 20/70.

Numerous requirements are formulated by the users, including mechanical properties (compression, tension, abrasion resistances, etc.), thermal resistance, the dry material/solvent ratio, life time and, of course, also the
5 quality/price ratio. Coating easiness, including in severe conditions of room temperature and relative humidity of the atmosphere, and risks and dangers during coating, must also be taken into account.

Aims of the invention

10 The present invention aims at providing a process and a composition suiting to those requirements and, particularly, improved means to protect efficiently against chemical reactants, particularly against chemical attacks, namely alkaline and mainly acid ones, external and internal
15 surfaces, particularly concrete tanks or steel tanks and containers as used generally in the chemical industry. Other applications can of course also be envisaged, such as building protections.

Characteristic features of the present invention

20 The invention relates to a process of protecting surfaces against corrosive materials, which consists in using a composition comprising a polystyrene, so-called impact-polystyrene, in a solution in an appropriate solvent, preferably in styrene, which is mixed in quantity of 1 to 18
25 parts, preferably approximately 4 parts, in weight of a vinyl or unsaturated polyester resin for one part in weight of the polystyrene solution, in the presence of accelerators or catalysts.

The polystyrene solution in the solvent thereof is
30 preferably in such a concentration that an appropriate (syrup-like) fluidity is obtained. Preferably the polystyrene/styrene ratio is approximately 20/70.

Preferably, catalysts of organic oxide type, such as methylethylketone peroxide (MEKP), are used which are well soluble in styrene and in most of the other solvents taken into account in the technique according to the invention.

5 In those conditions, polystyrene is bound with free radicals of vinyl resin, forming chains of such a length that they serve as a backbone in a matrix formed with the resin base, which has as a consequence that shrinkage upon setting becomes practically null or at least negligible, for example
10 approx. 1%.

Moreover, in those conditions, the thermal expansion values of the coating are very small and practically close to concrete ones. The mechanical and chemical resistance properties, particularly upon an exposure
15 to chemically aggressive agents, mainly acid or basic ones, are also unique.

Most of the commercially-available polystyrenes, particularly those having an improved impact resistance, of an average molecular mass M_n of about 100000 to 250000, of HI
20 Polystyrene 34400 type, can be used.

They are dissolved preferably in styrene until a state corresponding to the consistency of a syrup-like material is obtained, and mixed with the vinyl or the unsaturated polyester resin. Resins of this type are
25 preferably compounds selected from the group consisting of:

- orthophtalate or isophtalate polyester resins, or
- epoxy vinyl esters such as Novolac-epoxy based vinyl ester resins, bisphenol-A-epoxy based vinyl ester resins, brominated bisphenol-A-epoxy based vinyl ester resins
30 or rubber modified epoxy vinyl ester resins.

Typical products are sold in the shops in compositions form of the type DERAKANE ® made by Dow. Such

products are, among others, DERAKANE ® 470, 411, 411-400 and compatibles.

The quantity of catalyst particularly is dependant upon its nature and quantities and weight ratios of the above-mentioned components. It can be determined easily by people skilled in the art through a few orientation trials.

To implement the process, a "mortar" is made by adding an additive such as sand. Depending upon the nature of the added sand and the coating thickness, the proportion of sand used can vary from 1 to 20 parts, preferably from 4 to 9 parts of sand for one part of the composition according to the invention. Other additives may be used such as "glass flakes", or "glass linings". Furthermore, it is also possible but not compulsory to add a hydraulic binder or cement.

It has been shown that, when a non previously treated vinyl ester resin according to the invention is used to make an anti-acid coating on a cement concrete, enormous tensions appear between, on one part, the existing substrate (concrete), and, on the other part, the protective ester layer, the values of which can be expressed as follows :

- the module E of the vinyl ester resin, after setting, is about 300 N/mm².

Supposing that shrinkage occurs after a complete setting and consequently this shrinkage is restrained by the adherence with the concrete substrate, the theoretical tensions which can appear are :

$$\sigma = \epsilon E$$

$$\sigma = 0.08 \times 300 = 240 \text{ N/mm}^2.$$

That leads inevitably to a delamination of the untreated vinyl resin coating from the substrate thereof.

In reality, however, the shrinkage only appears

between the setting start (that is to say upon gelification) and the moment where a complete setting is reached. Supposing the shrinkage and the elasticity module are linear, stresses of about 13.6 N/mm² would be reached in the vinyl resin layer.

If it is considered that the tensile strength limit of the vinyl ester resin is about 15 N/mm², it will be observed that values of 13.6 N/mm² are quite close to this yield strength.

On the contrary, in the case of the composition according to the invention, shrinkage is reduced to 1% max, which reduces the stress upon setting to about 1.9 N/mm².

Moreover, upon setting, the residue styrene is reduced to a minimum, which assures wholly, at a long term, a well better stability compared to conventional compositions.

Tension trials on coatings according to the invention made on a concrete show systematically that a breaking of the concrete substrate occurs before its coating. It is to be noticed that, because of the very small yield module of the vinyl ester based resin, it is advantageous to load the composition according to the invention with fillers adapted for the substrate to be covered, so that the final product has a yield module similar to the substrate thereof.

The fact that the substrate and the coating have very close or similar thermal expansion properties, taking strongly reduced shrinkage stresses into account, assures a unique mutual adherence.

For the product according to the invention, the following characteristics have been measured.

Table I

Physical properties	Digital value
<u>A. Specific properties of pure resins at 25°C</u>	
Specific mass	1.10
Brookfield viscosity	200
Flash point (°C)	32
Maximum acid number	11
Styrene content (%)	40
<u>B. Properties of a cast clear mass at room temperature</u>	
Compression strength (N/mm ²)	127
Tensile strength (N/mm ²)	73
Flexural strength (N/mm ²)	133
Flexural module (N/mm ²)	3800
Barcoll hardness	40
Average expansion coefficient between 25 and 100°C (X / 1000000 cm / cm /°C)	53
Thermal distortion temperature (°C)	145

The resin according to the invention can be applied as a cover on monolithic coatings.

The coating is carried out preferably in the following working conditions :

- temperature of the working zone > 5°C
- temperature of the concrete or cover material > 5°C
- relative humidity < 70°C
- the dew point of the material which receives the treatment should be adapted (3°C above the dew point)

- the working surface must be dry and dust-free
 - other contaminants such as previous cover materials, greases, oils, waxes, etc. should be removed
 - a previous appropriate cleaning of the surface is of course
- 5 to be recommended, such as sanding, scratching, etc. by removing the residue materials.

The primer can be easily applied by any appropriate technique, by blade, brush, roll or gun coating.

The resin is then coated preferably on such a

10 primer by techniques convenient for its consistency. In particular, when the resin forms an aggregate loaded with silica sand and mixed with a flame retardant (alumina trihydrate), the coating can be effected with a trowel with a thickness of 15 to 20 mm depending upon the required

15 resistance.

It is particularly recommended to apply a glass fiber mat of 300 gsm between the primer and the resin coating. The glass fibers are preferably randomly-oriented fibers of 50 mm length. It is advantageous to press the wet

20 resin with a roll so as to impregnate the glass fibers. The glass fiber mat is applied as successive parallel stripes of 120 mm with overlappings of 50 mm at the joints. Possibly additional quantities of resin are added to humidify completely the whole glass fibers. When all the glass fibers

25 are so wetted, the surface is worked with a roll or another equipment convenient to remove any captive air bubble.

In the following Table II, mechanical properties of various mortars have been compared. Comparison has been made on one part with a conventional Portland cement, an

30 epoxy polyamide mortar with 4.5 parts sand, and a mortar according to the invention with 6 parts sand (columns A, B and C, respectively).

Table II

Mechanical properties of different mortars			
	A	B	C
Compression strength N/mm ² (psi)			
5 1 day		41 (6000)	103 (15000)
2 days	10 (1500)	69 (10000)	
7 days	24 (3500)	90 (13000)	110 (16000)
28 days	31 (4500)	97 (14000)	117 (17000)
Tensile strength N/mm ² (psi)			
10 1 day		8,3 (1200)	20,7 (3000)
2 days	1,4 (200)	15,2 (2200)	
7 days	2,1 (300)	20,7 (3000)	22,1 (3200)
28 days	2,8 (400)	22,1 (3200)	22,8 (3300)
Flexural strength N/mm ² (psi)			
15 1 day			34,5 (5000)
7 days		45,5 (6600)	37,9 (5500)
28 days		45,5 (6600)	41,4 (6000)

Example 1

20 A resin DERA KANE® 470 is mixed in quantity of 4 parts for one part of polystyrene in styrene in the ratio 20/70 (composition A).

Upon implementation, 1.5%-3% of accelerator (B) such as 1% cobalt in phthalate plasticizer or an amine
 25 accelerator such as 10% DMA, DEA or DMP are added. After mixing, 2% of a hardener (C) which is a catalyst of the type benzoyl peroxide, cumene hydroperoxide or an other MEKP is added.

The preparation can be coated directly by any
 30 appropriate means (roll, brush, ...) in quantity of 350 gsm on a clean and smooth surface, for example, concrete, forming

a wall, a ground or a tank.

After about one hour drying (setting), the surface may receive a mortar.

Said mortar is prepared as follows :

5 In a mixture of composition A with 2% hardener B in a Zyclos or BEBA type mixer, 1 part of the mixture A + B and 9 parts of the component C formed with an acid-cleaned dry mixture of quartz sand granulate are measured. The coating of this mortar, with a final smoothing, is carried
10 out professionally up to a thickness of 10 mm in a vertical application.

Example 2

Composition A is identical to composition of example 1, except for an addition of an appropriate quantity
15 of a thixotropic agent.

After about one hour drying time, a mortar is formed this time by mixing 1 part of the above-mentioned mixture A + B with 4 parts of C.

This mortar may be applied through a trowel or a
20 spatule and a smoothing plate in a thickness up to 5 mm. However, a smoothing of the irregularities reaching up to depressions of 15 mm can be carried out with no difficulties.

For coating concrete, resin compositions intended for horizontal application of respectively 15, 10 and 5 mm
25 can be made of a mixture resin / quartz sand with a weight ratio of 1/9, 1/7 and 1/5.

In a vertical application of 5 mm thickness, a ratio of 1/4 is most suitable.

It is also possible to use a mixture of resin and
30 glass composites (flakes or glass mats or else) in a ratio 1/2 which is suitable for concrete and metal coating.

C L A I M S

1. Process of protecting surfaces against corrosive materials, characterized in that a composition is used, comprising a polystyrene, so-called impact-polystyrene, in solution in an appropriate solvent, preferably in styrene, which is mixed in quantity of 1 to 18 parts, preferably approximately 4 parts, in weight of a vinyl or unsaturated polyester resin for one part in weight of the polystyrene solution, in the presence of accelerators or catalysts.

2. Process according to claim 1, characterized in that the polystyrene solution in the solvent thereof is preferably in such a concentration that a syrup-like fluidity is obtained.

3. Process according to claim 1 or 2, characterized in that the polystyrene/styrene ratio is approximately 20/70.

4. Process according to any of claims 1 to 3, characterized in that the composition contains organic oxides such as methylethylketone peroxide (MEKP).

5. Process according to any of claims 1 to 4, characterized in that the vinyl resin is selected from the group consisting of:

- orthophthalate or isophthalate polyester resins, or
- epoxy vinyl esters such as Novolac-epoxy based vinyl ester resins, bisphenol-A-epoxy based vinyl ester resins, brominated bisphenol-A-epoxy based vinyl ester resins or rubber modified epoxy vinyl ester resins.

6. Process according to claim 5, characterized in that the DERA-KANE® resin is of the 470 series for cement concrete coating and of the 80084 type for metal coating.

7. Product as a mortar to carry out the process according to any of claims 1 to 6, characterized in that the



proportion of sand is in the range from 1 to 20 parts, preferably from 4 to 9 parts of sand for one part of said composition.

A B S T R A C TPROCESS FOR PROTECTING SURFACES AGAINST CORROSIVE
MATERIALS AND RESIN BASE PRODUCTS THEREFOR

5

Process for protecting surfaces against corrosive materials, characterized in that a composition is used, comprising a polystyrene, so-called impact-polystyrene, in solution in an appropriate solvent, preferably in styrene, 10 which is mixed in quantity of 1 to 18 parts, preferably approximately 4 parts, in weight of a vinyl or unsaturated polyester resin for one part in weight of the polystyrene solution, in the presence of accelerators or catalysts.

9706111-3**04 JUN 1997**