

PROTECTION OF SURFACES OF NATURAL STONE AND CONCRETE THROUGH POLYMERS

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ABSTRACT

Due to the ever increasing rate of decay, the conservation of building material calls for the use of modern processes. Above all "reactive systems" and polymers lend themselves to this purpose. They replace lost bonding agents in the material, provide a connecting bond for fissures, protect the upper surfaces against aggressive media and enable more weather-resistant workpieces to be manufactured. By natural stones the weathering requires often a treatment with a stone strengthener before hydrophobizing the stones. Only a prehydrolyzed silicic acid ethyl ester can be applied safely and gives better results in consolidation than the monomer ester. The Poly-Silicic-Acid-Ethylester reacts with the water absorbed at the capillary walls and silicic acid gel is formed. In the past years, this technology was been used on many objects in Europe, including the works in the Forum Romanum in Rome, the reconstruction of the Greek Theatre, part of the temple of Apollo Licio in Metaponto in the south of Italy and this year on buildings in Petra. A description is given of the systems tested for this purpose.

1 INTRODUCTION

The attack over the surface is mainly caused by water and dissolved harmful substances in it. Water has also on concrete a precipitant effect on the carbonatisation through CO_2 . The protection of the surfaces of buildings was mainly attempted through paints, but very often the most important physical-building rules, e. g. water vapor permeability, have not been taken into consideration.

In the past years many monuments were destroyed more due to the wrong methods of treatment and insufficient materials than through environmental damage.

But the chemistry offers possibilities for a very effective and long-lasting protection of the materials and therefore also of the buildings from water and it's harmful substances.

Through proper treatment of the surfaces of natural stones, concrete and a selection of products, one can achieve to the greatest possible extent, e.g. to water vapor permeability, needed for the requirements. This can be either an

impregnation with monomer silanes, reacting with the inner surface of the material to polysiloxanes, or a coating with a mortar with a reacting resin as a binder.

By an impregnation only the water vapor permeability is hardly influenced; compared with coating, where it becomes watertight. In addition to the physical consequences of a treatment of the surfaces, the chemical property of the used products must also be taken in consideration. In contrast to concrete, there occurs with the weathering of natural stone a loss of binder, which causes a reduction of the stability.

The modern restoration grants every building the right of being old. Therefore, it is necessary to restore the lost binder in the natural stone and so the stability. The achieved profile of consolidation must be the same as for the not yet effloresced stone. Is this not the case, tensions arise and crackings and cracking-offs are the consequences. The loss of old material would be larger than before the treatment. In order to avoid this, the poly-silicic acid ester must penetrate deeply and must not be catalyzed.

2 HISTORY

The protection of monuments and buildings made of natural stones is not a development of modern times, it has been used since millenniums. Probably the oldest description of a chemical provision for the protection of a monument can be found in the Bible:

"Jacob got up early next morning, took the stone that was under his head, and set it up as a memorial. Then he poured olive oil on it".

As an example for mechanical protection of a building we can look at the pyramids in Gizeh. The Cheop's pyramid, raised from 2551 till 2528 B. C. is covered with plates made of Tura limestone, which remained till today, except the damages done in the Middle Ages, where these plates were used as building material.

We know from Plinius the Eldest (24 -79 A. C.):

"Marble needs great care, although it has a good durability".

In the antiquity the stones were treated with linseed oil or hot wax to protect the surface from the access of water. We come to the following conclusion:

"RAIN PROTECTION IS PRESERVATION OF MONUMENTS".

This is possibly due to chemical methods, structural precautions or combination of both. As another example for structural precautions, we can look at gargoyles on churches, still in use today; their purpose is to keep rainwater away from the

wall.

We will only talk here about chemical protective measures.

Up to the 19th Century it was common to give buildings, made of natural stones, a protective coat. This could be either of plaster, distemper or paint. The paints were based on oil-colour, tempera, casein or lime casein. Casein, the most important protein component of milk, was used since the antiquity as a bonding agent for inorganic pigments. Lime casein is formed out of casein and lime milk and produces a tough waterproof painting for outside walls. A combination with alkaline oil colour was possible. So each component was protected on the surface. The paintings used to be, according to the surroundings, coloured or monochrome. During the 19th Century, the Romantic period discovered the natural beauty of the colours and structures of natural stone. Two circumstances have come together, speeding up the decay: the renunciation of the protective coat and the beginning of the industrialization.

The knowledge of Winkler [1] , that the destruction of surfaces of natural stones since the beginning of the industrialization has speeded up rapidly, has been corroborated everywhere.

3 PRESERVATION

New, simple methods therefore had to be developed for renovation purposes; in other words, an overall concept per-mitting an historic property not only to be renovated but also to be restored. This is being helped by a rethinking in the field of future monument maintenance, inasmuch as the aim now is to retain as much of the old building material as possible. No fresh damage should be caused by the renovation measures, either. Until recently, only two alternatives were known to the building specialist as regards the conservation of old buildings and monuments: Rebuilding the damaged areas of the natural stone, and replacing defective natural stonework with new natural stone. A building renovated via this customary manual method looked like new at the end of the work, and there was no more worry for the next 30 - 40 years. Each generation carried out one renovation. This situation has altered in recent years due to environmental damage, and the interval before the next renovation becomes necessary has shrunk to 5 - 10 years. Not only is this linked with an enormous rise in costs, but - as experienced in Bern, for example - there are not enough masons available for this work. Damage therefore occurs more rapidly than renovations can be carried out.

immediately or in future. Without going into the details of damage analysis, there should be discussion of the products which are envisaged for renovating historic buildings. [2]

A pre-requisite for the use of the systems described above is that overall conditions and climatic surroundings of the object to be renovated be taken into account; basic damage analysis and preliminary tests on the original materials must also be carried out.

APPLICATION

TABLE 1
Survey of the various systems and their applications

	Impreg- nation	Pain- ting	Coating	Injec- tion	Polymer- concrete
PMMA-solutions	+	+			
PMMA + Silanes	+	+			
Silanes	+	+			
Poly-silicic acid est.	+				
PUR-systems	+	+	+	+	+
EP-resins mod.		+	+	+	
PMMA-resins	+	+	+	+	+
EP-resins pure			+		+

4 PMMA-SOLUTIONS

The solutions of polymethylmethacrylate, or of the copolymers are employed as raw materials for paints, are mass-produced by the chemical industry, by a hot-setting process: They thus contain no aromatic residue of the starter system and are therefore absolutely non-yellowing, at the same time showing excellent UV-resistance. Special types of polymers are used dissolved in appropriate solutions, and become effective after evaporation of the solvent by forming films of varying strength. This is regulatable according to the choice of concentration and the number of applications. As these PMMA-films are permeable to water vapor but resistant to air-borne pollutants. We are using a special modified polymethyl-butyl-copolymer with reactive groups.

TABLE 2

Diffusion Resistance Number [3] of MOTEMA®-FINISH		
μ CO ₂	=	6 100 000
μ H ₂ O	=	11 000

This product reduces the carbonatization of concrete, without reducing the water vapor permeability. It can also be pigmented. It is used with great success also

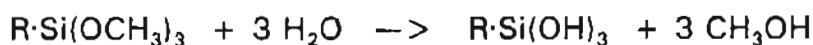
as a protective paint for paintings, frescoes, marble, gold-platings and for preserving stonework. [4] After all these good results and experiences, it was obvious to combine this product with silanes.

PMMA-solution + Silanes = MOTEMA®-FINISH-SIL

A combination is also possible with the silanes, and so PMMA-solutions also match the reactive system. Its test results are shown together with those of silanes.

Silanes

This silicon compound contains ester groups which form silanols during hydrolysis:



This alkyl-silanol is not stable and reacts immediately with another molecule, but also with OH-groups in the building material - which every silica building material contains - with a dehydration - process taking place. In this way, the silanol molecule becomes cross-linked or linked with a silicon atom in the building material. Through the intermediate stage of siloxanes, polysiloxanes (silicon resin) are then formed. These now show an excellent water-repellent finish, and protect the building material from penetration by water and the pollutants dissolved therein. At the same time, however, there is only an insignificant reduction in water vapor permeability.

Through the use of monomeric silanes with a molecular length of approx. 10 Å, deep penetration into the material is made possible. Gel pores in concrete have an average size of 25 Å, the percentage in cement stone runs up to 20 - 30% per vol. Polysiloxanes (silicon resins) have a molecular length between 150 and 1000 Å, so they are too large for gel pores. Also silicon resins do not fit in the capillary pores, connecting the gel pores, because the capillary pores measure 10 - 100 Å. The capillary absorptive capacity is reduced drastically through hydrophobizing. Thereby the frost-resistance has been fundamentally improved and the penetration of harmful substances e.g. chloride-ions is stopped effectively. This applies to concrete as well as to natural stones. Due to the hydrophobizing, the steel corrosion in concrete is stopped. It can not be excluded, that the carbonatization in fresh concrete is speeded up slightly. Therefore also here a combination with MOTEMA®-FINISH. The depth of penetration and the effectiveness was specified on DIN-standard-mortar 0 - 6 mm. They verified:

- the water absorption coefficient A,
- the depth of penetration through grinding off and repeated examination,
- the alkaline resistance through an exposure (14 days) at +60°C in saturated calcium-hydroxide-solution.

TABLE 3

Water Absorption Coefficient A:		kg / m ² · h ^{0,5}	
		Silane	FINISH-Silane
Mortar untreated		0,200	0,200
Mortar surface treated		0,038	0,039
grind-off	: - 1 mm	0,054	0,057
	: - 2 mm	0,055	0,067
	: - 3 mm	0,094	0,649
after 14 days Ca(OH) ₂ + 60°C		0,057	0,053

The water absorption coefficient A is reduced by MOTEMA®-Silane by 5,3 times and by MOTEMA®-Finish-Sil by 5,1 times. The alkaline resistance exists.

TABLE 4

Water Vapor Diffusion Resistance Factor:		kg / m ² · h ^{0,5}	
Mortar untreated		0,150	
Silane treated		0,029	
FINISH-Silane treated		0,029	

The water vapor diffusion resistance factor is 81% under the value of the untreated sample.

TABLE 5

Equivalent of Diffusion Resistance Factor: Sd in m			
Mortar untreated		0,75	
Silane treated		0,75	
FINISH-Silane treated		0,74	

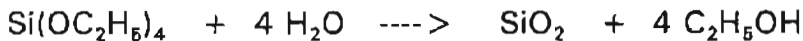
TABLE 6

Product Sd . A:	μ 50 - 100
Mortar untreated	60
Silane treated	60
FINISH-Silane treated	59

The fundamental demand for a hydrophobising: no change of the water vapor permeability is met by both products. [5]

Silicic acid esters

In large parts of central Europe, the most frequently used natural stone is sandstone. The bonding agents holding the individual sand granules together are washed out over the course of years, with the result that the sandstone loses its firmness. In order to retain as much as possible of the building substance, it is now necessary to replace the lost bonding agent, i.e. to compact the sandstone. Silicic acid ester reacts, as follows with water:



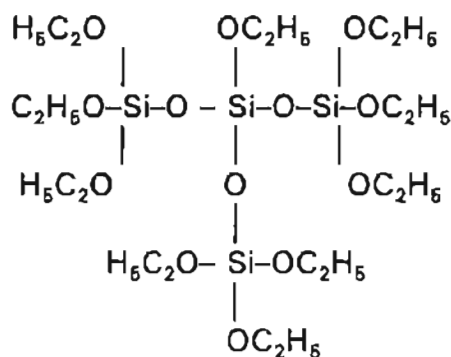
Through hydrolysis, an anorganic "polymer" is produced here from an anorganic ester. Silicium dioxide is the purest quartz; the ethanol (ethyl- alcohol) which comes about as a by-product is not damaging either the building material or the building structure. Of importance is the fact that the hydrolysis of the silicic acid ester only takes place slowly, so that the silicic acid ester can penetrate deeply into the stone to be strengthened; only in this way can a uniform degree of strength be achieved. In no event may the silicic acid ester be so reactive that it already reacts in the upper level, causing a shell to be formed. The penetration should therefore be evident for up to a depth of 50 mm. Serious differences of the stability profile, e.g. a rapid decrease of the effectiveness in already a depth of 40 mm [6] as it occurs by a catalyzed silicic acid ethyl ester, have not been found in any of the numerous tests. Because the large pores remain unfilled, the porosity and so the important water vapor permeability is preserved.

The monomer silicic acid esters had already been on the market for more than 10 years in 1978, when our customers asked for a slowly hydrolyzing stone strengthener. Chemistry prescribes an increase in pressure and temperature as a means of accelerating chemical reactions. Both are out of question for stone consolidation.

A polymerization at room temperature proceeds substantially quicker, if the first phase takes place in advance in a separate reaction before remixing prepolymerisat with the monomers. This reaction is accomplished in the workshop by increased temperature. We examined whether the Trommsdorf-effect is also applicable by silicic acid ethyl ester after pre-hydrolysis.

In test series, the most favourable relation between viscosity and reactivity were determined. We found an oligomer consisting of an average of 4 molecular

components to be especially suitable. The structural formula can be presumed as follows:

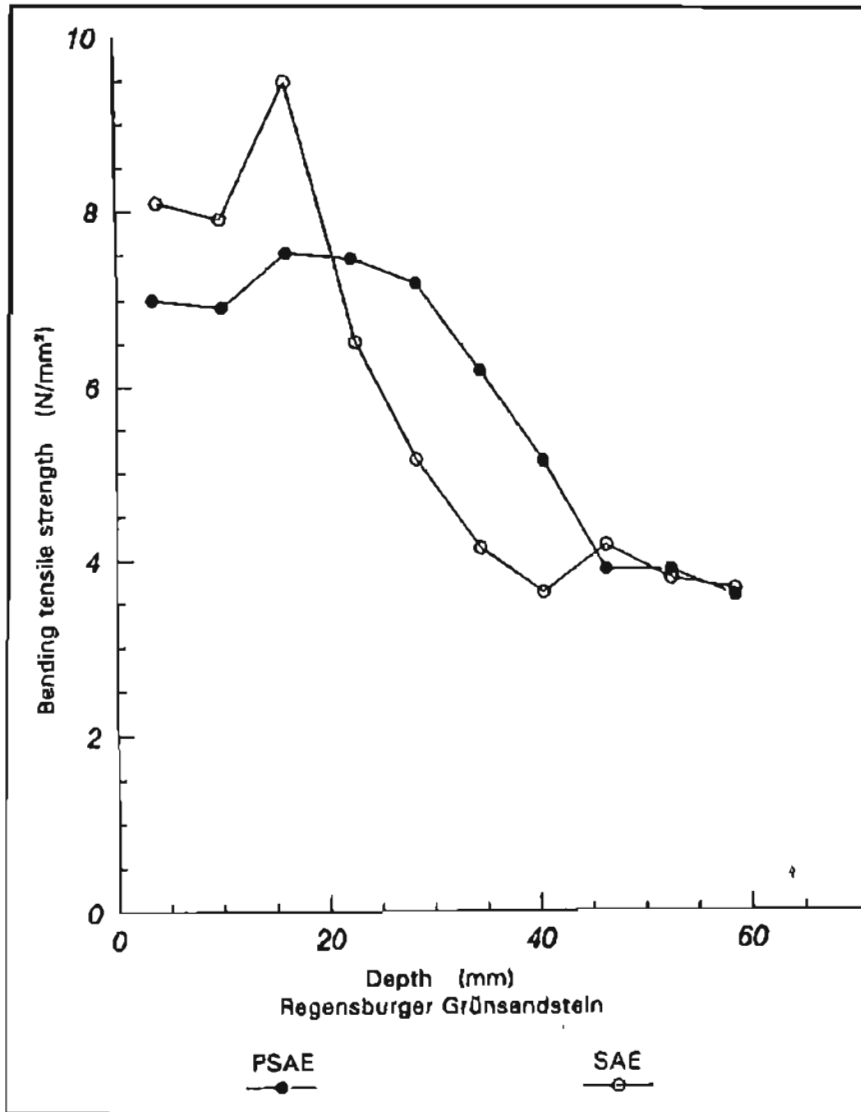


This oligomer has an average molecular weight of appr. 650 and a SiO_2 -content of 40 to 50 % w/w. The viscosity rises from 1 mPa·s of the monomer ethyl ester to 5 mPa·s, which is still acceptable. The increased viscosity can be reduced by adding a solvent. This is necessary anyway, because a stone strengthener with an SiO_2 -content of 40 to 50 % w/w should not be applied. [7]

How can the secretion "in situ", i.e. in the depth of the stone, be controlled? On every crystal surface in a stone and particularly on quartz there exists a stratum of water molecules. This so-called Helmholtz-Stratum has a strength of appr. 3 molecule layers. There is a zone inside the stone which contains water and which is required for the hydrolysis of the poly silicic acid ester. The enrichment of water can be additionally supported by using a hygroscopic solvent, such as ethanol. Ethanol has a boiling point of 78°C, can be combined with silicic acid (ethyl) ester products as well as with water in every proportion and is physiologically harmless.

The slower hydrolysis in comparison with the catalyzed silicic acid ester was accepted intentionally, because it has a decisive advantage: during the hydrolysis of ester a relatively large amount of ethanol has to escape from the system. The consequence is a strong shrinkage and high tensile strength which are caused in the gel. During the hydrolysis of a silicic acid ester, silanole are developed as an intermediate stage. This becomes apparent through a passing hydrophobic stage on the consolidated stone. If the gel exists as a silanole for a longer time and if during this stage a large amount of ethanol can be separately evaporated, the shrinkage of the gel is substantially diminished after the complete hydrolysis and dehydration. Tension is reduced and the consolidations are more uniform. This is shown in the following diagram. The non-pre-condensed, high catalyzed product shows a rough increase of the consolidation towards the surface. The pre-condensed product on the other hand has a well-balanced consolidation profile with a smooth inward course. [8]

FIG.1



In 1978 we did not pay attention to the safety-relevant data of the monomer tetra ethyl silicat (silicic acid tetra ethyl ester), because we did not intend to use a monomer ester as a stone strengthener.

On the market "solvent free" stone strengtheners are offered as very environmentally safe. This means a solvent free, catalized silicic acid tetra ethyl ester. We have examined the possibility of the combination of a polyester within the monomer ester as a solvent, in order to be able to offer also a solvent free stone strengthener. To do this, we had to consider safety-related data. We determined that the MAC of tetra ethyl silicate is only 20 ppm, but that it has no odour before 85 ppm. This means that one can inhale a toxic amount before noticing any odour. The following table compares the most important safety-relevant data of silicic acid ethyl- (SAE) and poly silicid acid ethyl esters (PSAE) . [9] [10]

	SAE	PSAE
Danger symbol:	Xn, = hazardous	none
Possible dangers:	flammable, hazardous by inhalation, irritates the eyes, respiratory organs and skin.	no particular dangers known

Polymer Concrete (PC)

Many different problems arise in connection with renovation, and these also require different products. Only EP and PUR resins permit the manufacture of porous, i.e. water vapour permeable systems, synthetic substitute stone materials. MMA resins are not suitable to this purpose, because these do not polymerize due to oxygen inhibition. [11]

TABLE 7

Reactive Resins (DIN 18 557) for Polymer Concrete (PC) and Coatings	
Epoxi resins	EP
Methacrylic resins	MMA
Polyester resins (unsaturated)	UP
Polyurethane resins	PUR

Epoxi resins harden by polyaddition; i.e. by separation of the epoxide groups and by addition = addition of accelerators with active hydrogen atoms. Resins and accelerators must be dosed in stoichiometric amounts. The hardening reaction is temperature-dependent. Due regard must be paid to the fact that there are no non-yellowing epoxi resins and, if they are for example used in weather-exposed areas, that the stone replacement materials made from them must be weatherproofed with silanes

Methacrylic resins are distinguished from all the other reaction resins by the fact that in its case monomeric methylmethacrylate is already polymerisable with a viscosity of 1 mPa·s (identical to water). If required, however, the viscosity can be set at any desired level by means of dissolving polymethacrylates. A further advantage of MMA resins is their high reactivity, even at temperatures of 0° C and below. For special applications like synthetic white marble, we have now a redoxsystem without any yellowing.

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Polyurethane resins harden through polyaddition, and, as a rule, form elastic polymers. The hardening is strongly catalyzed through moistness. Using aliphatic isocyanates in conjunction with aliphatic poly-alcohols, light- and weatherproof polyurethane systems are produced. The resistance to UV has to be improved by adding UV- inhibitors.

5 CONCLUSION

The destruction of surfaces of natural stones and concrete has speeded up rapidly and can be corroborated everywhere. The attack on the surface is primarily caused by water and in it dissolved harmful substances. In past years many monuments were destroyed more due to the wrong methods of treatment and insufficient materials than through environmental damage. But the responsible chemistry offers possibilities for a very effective and long-lasting protection of the materials and therefore also for the buildings and monuments.

The alternative is to do nothing and wait the further dilapidation of the monuments.

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