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Polyurethane Prepolymers for the Protection and Conservation of Natural Stones

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Abstract

A stone protecting agent was developed by introducing new modified isocyanate monomers. Treated natural stones show a high impregnation depth of the agent as well as good water repellent properties. The stone is strengthened and the water vapour diffusion is lowered only to a low extent. A main aspect of the new development was the consideration of working safety aspects. The toxicity could be kept low by the use of the new monomer types.

Keywords: isocyanate, vapor diffusion, toxicity

1 Introduction

To retard the deterioration of capillary porous stone buildings and sculptures, cold curing polymer systems which build up a protective micro-layer on the inner surfaces of the stones in order to strengthen and protect the porous structure without stopping the transport processes of water vapour through the pores are developed. The concept of open-pore polymer impregnation, the so called "Aachen Concept" [1], was published earlier. The principle is shown in Figure 1.

Protective agents which are designed for the "Aachen Concept" have to fulfil many very diverse demands. The chemically and technically oriented requirements can be summarized by the following criteria:

- cold curing (complete crosslinking/hardening at temperatures above 10 °C),
- low viscosity (less than 10 mPa×s),
- slow viscosity increase over a period of several days,
- filmforming,
- entropic elasticity of film,

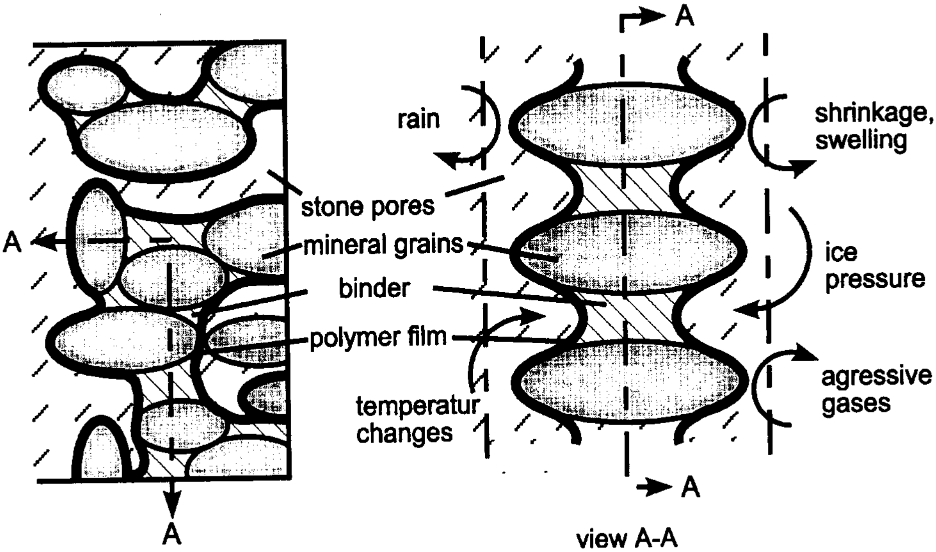


Figure 1: Schema of the „Aachen Concept" of stone conservation

- 20 to 30% content of active agent,
- low toxicity.

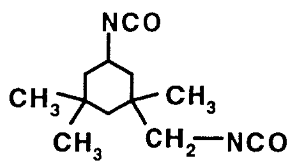
The development of polyurethane based agents, which fulfil these demands, is presented in the following. Their chemical formulation and the properties of natural stones, treated with these agents, will be discussed.

2 The polyurethane system

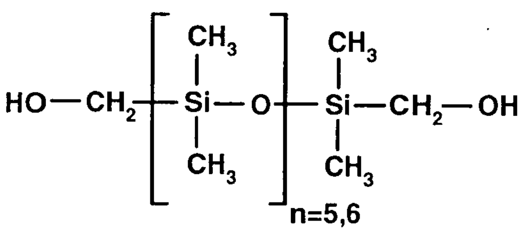
The polymer polysiloxane modified polyurethane films are formed by solutions of polyurethaneprepolymers, which can penetrate the stone pores [3, 4, 5]. After evaporation of the solvent, the prepolymeres cure by reaction with humidity present in the stone.

The prepolymeres are synthesised by reaction of monomers like isophoronediisocyanate (I) with bishydroxyfunctional polysiloxanes (II).

(I)

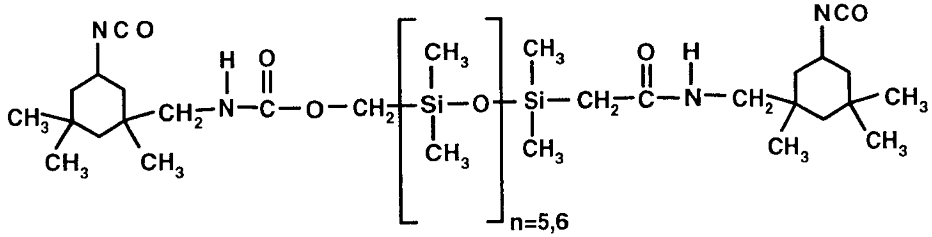


(II)



The idealised structure of the prepolymeres is shown in (III).

(III)



The capability of moisture curing is given by the isocyanate-(-NCO)-groups. This reaction leads to polyurea structures. The scheme of the reaction can be given as follows:

$$R{-}NCO + H_2O \longrightarrow R{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH \longrightarrow R{-}NH_2 + CO_2$$

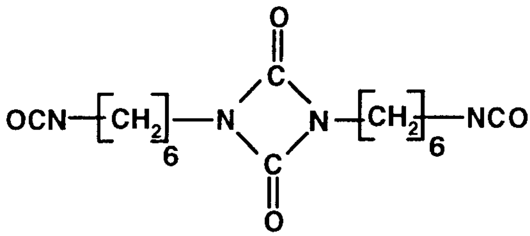
$$R{-}NCO + R{-}NH_2 \longrightarrow R{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}R$$

The isocyanate groups of the prepolymer (I) reacts with water yielding the amine V. The amine itself reacts with another isocyanate group. This leads to the urea structure (VI), which links two prepolymers. By performing this reaction over and over, a crosslinked polymer film is formed.

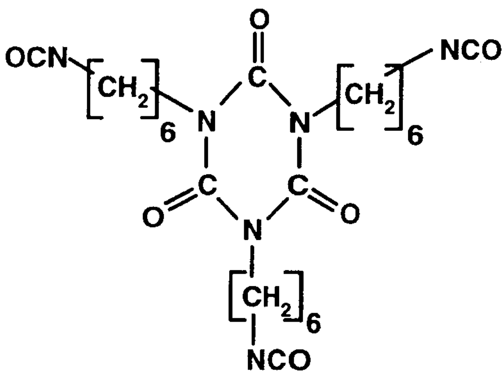
With this short description it is clear that the discussed prepolymers can easily react in cross-linking-reactions. Semiprepolymers, which contain additional isocyanate monomers, are even better cross-linkers. On the other hand high contents of free isocyanate monomers are not desired due to toxicological considerations.

This problem was solved by introducing high-cross-linking but low volatile isocyanates [6]. Specially useful as a substitute for free isocyanates in the prepolymer are the trimer (VIII) and the dimer (VII) of hexamethylenediisocyanate (IX) with the following structures.

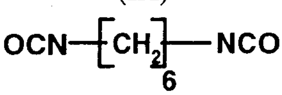
(VII)



(VIII)



(IX)



The stone protecting agents which are described here, consist of mixtures of the prepolymer (III) and the modified isocyanates (VII) and (VIII). The composition of the two tested mixtures is given in table 1.

The table 2 is an overview of the most important properties of the fluid protecting agents (content of solids, viscosity, surface tension), the glass temperature of hardenend polymer films and the material uptake during the impregnation of two typical german sandstones.

Table 1: Composition of the stone protecting agents

agent	content of		
No.	III	VII	VIII
	M.-%		
1	2	3	4
219	24,5 (n = 6)	1,3	0,9
221	24,7 (n = 12)	0,75	0,5

Table 2: Properties of the fluid impregnation agents, glass transition temperature (TG) of the polymer film and material uptake during the impregnation of Sander Sandstone (SS) and Ebenheider Sandstone (EH)

agent	content of solids	viscosity	surface tension	T_G	material uptake SS	material uptake EH
No.	M.-%	mPa·s	mN/m	°C	Kg/m²	Kg/m²
1	2	3	4	5	6	7
219	26,4	2,1	23,7	42	1,6	2,8
221	26,7	2,3	24,9	-105	1,7	2,5

3 Experimental

The substrate, on which the experiments are carried out, are samples of two different types of sandstones, representative for German stone monuments, Ebenheider Sandstone (EH) and Sander Schilfsandstone (SS). The stone samples used have the dimensions of $50 \cdot 50 \cdot 100$ mm^3. The samples' lateral faces are sealed by an epoxy-resin to prevent water or solvent from evaporation whereas the front faces remain free. The stone protecting agents are applied by capillary suction. The samples are immersed into the prepolymeric solution or emulsion under atmospheric pressure for 2 hours. The material uptake was determined gravimetrically. Then the stones are left for drying in laboratory climate of 23 °C/50 % relative humidity. After allowing 28 days for hardening of the polymeric film in the stone, a core of the diameter 44 mm was drilled out of the samples, followed by cutting it into slices of 4 mm thickness.

The mechanical and hycric data were determined using the slices. Water uptake was measured gravimetrically by allowing 1 hour capillary suction of the slices in deionized water. Watervapor diffusion coefficient was determined according to german standard DIN 52 617 by the wet-cup method.

The determination of the mechanical parameters modulus of elasticity and strength was carried out by testing the biaxial bending strength of the stone slices. The method was carried out according to literature [5].

4 Characteristics of the treated stones

The characteristics of the compound material stone - hardened polymer agent are the deciding criterion for the judgement of the effectiveness of the treatment. Water uptake and water vapor diffusion of the treated stone in comparison to the untreated areas are parameters for the hygric characteristics, changes in bending strength and modulus of elasticity are important for the judgement of the mechanical properties.

4.1 Hygric Properties

Figure 2 shows the capillary water uptake of Ebenheider Sandstone, treated with the agents No. 219 and 221, as a function of the depth of stone measured beginning with the impregnated surface.

The reduction of water uptake is most obvious when comparing the surface region of the stone with the untreated region at ca. 90 mm depth of stone. Both agents decrease the water uptake of the stone surface - which is most important on site - to less than 5 % of the value of the untreated stone. The agents are to be judged as very hydrophobic by this. The graph of the water uptake in the regions of the stone between the surface and the untreated area is on a lower level for the agent N. 221 than for the agent No. 219. This can easily be explained by the higher content of hydrophobic methylesiloxane structures in the agent No. 221.

The open pores of the natural stone shall not be shut by the impregnation measure, in order to avoid a reduction of the water vapor diffusion. Obviously, a hydrophobic agent reduces the water vapor diffusion even if the

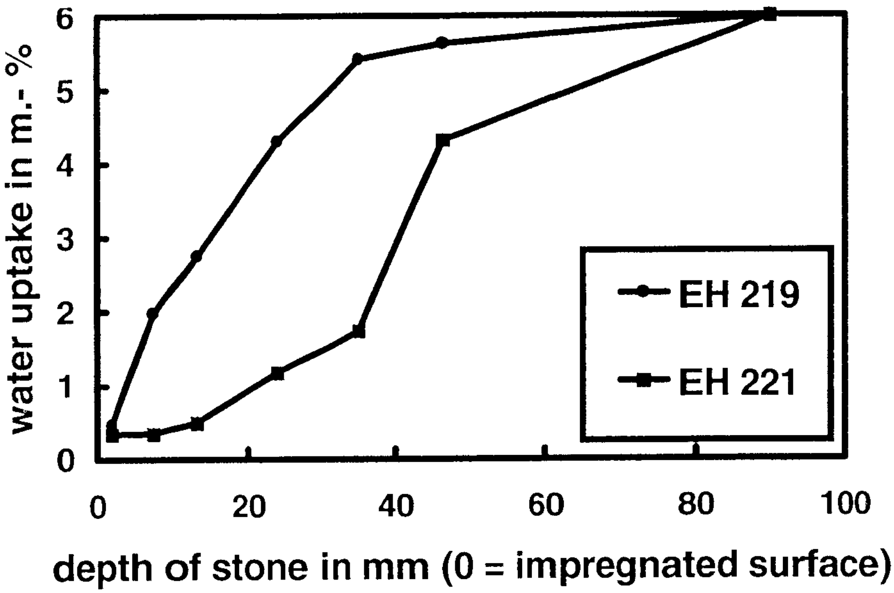


Figure 2: Capillary water uptake of Ebenheider Sandstone, treated with the agents No. 219 and 221 as a function of the depth of stone.

pores remain completely open by hindering one component of the water transport process. Nevertheless, this reduction should be kept on a low level. Water vapor diffusion coefficient μ, which was measured using stone slices, is the deciding parameter.

Figure 3 shows the water vapor diffusion coefficient μ for Ebenheider Sandstone und Sander Schilfsandstone, both treated with agent No. 219. The value for the untreated stone can be seen at 90 mm depth of stone again. The water vapor diffusion coefficient rises by a factor of 2,5 for Ebenheider Sandstone and a factor 2 for Sander Schilfsandstone, which means, that the water vapor diffusion itself is reduced by this factors.

4.2 Mechanical Characteristics

Another main criterion of the effectiveness of a protective agent are the strengthening properties, if a consolidation of the stone is desired. If a deteriorated, weak stone has to be strengthened, this strengthening by a protective agent should reach into the sound bulk of the stone.

Determination of the mechanical characteristics of stones treated with the agents reported here, shows that a strengthening effect up to a depth of

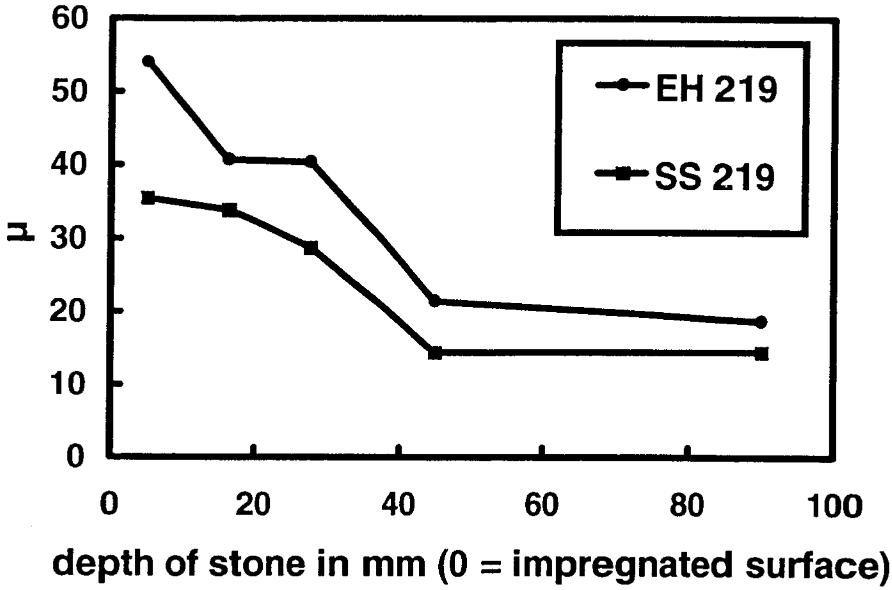


Figure 3: Water vapor diffusion coefficient μ for Ebenheider Sandstone und Sander Schilfsandstone, both treated with agent No. 219

stone of 35 mm can be achieved. Figure 4 shows the bending strength of Ebenheider Sandstone, treated with the agents No. 219 and 221. The mean value of five individual values is displayed. It can clearly be seen, that the bending strength of the untreated stone is lower compared to the treated samples. The degree of strengthening performed by the two tested materials differs only in the first few millimeters of stone depth.

Figure 5 shows the modulus of elasticity of Ebenheider Sandstone, treated with the agents No. 219 and 221. The mean value of five individual values is displayed. Agent No. 221 causes a slighly more moderate increase of the modulus of elasticity in comparison to agent No. 219. This is not surprising, as the longer siloxane chain of agent No. 221 leads to a much softer polymer film than the shorter chain of agent No. 219. Also the glass transition temperatures of the two films are different (table1).

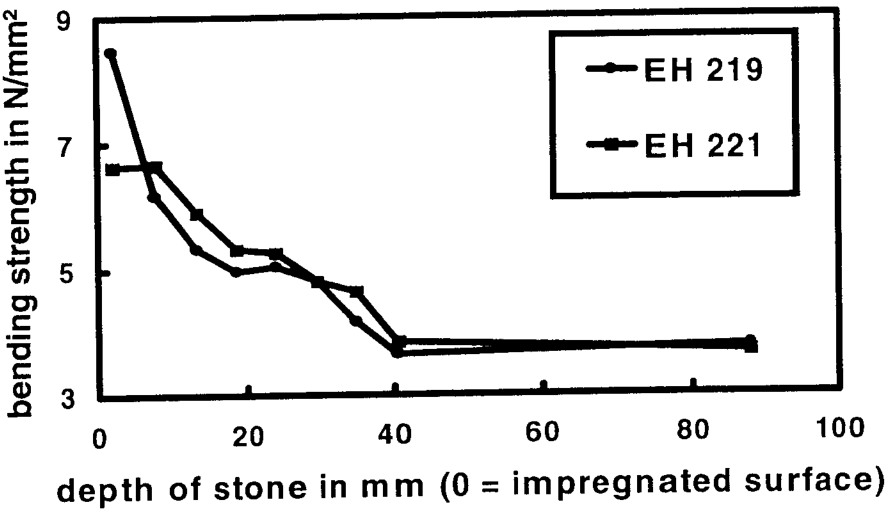


Figure 4: Bending strength of Ebenheider Sandstone, treated with the agents No. 219 and 221

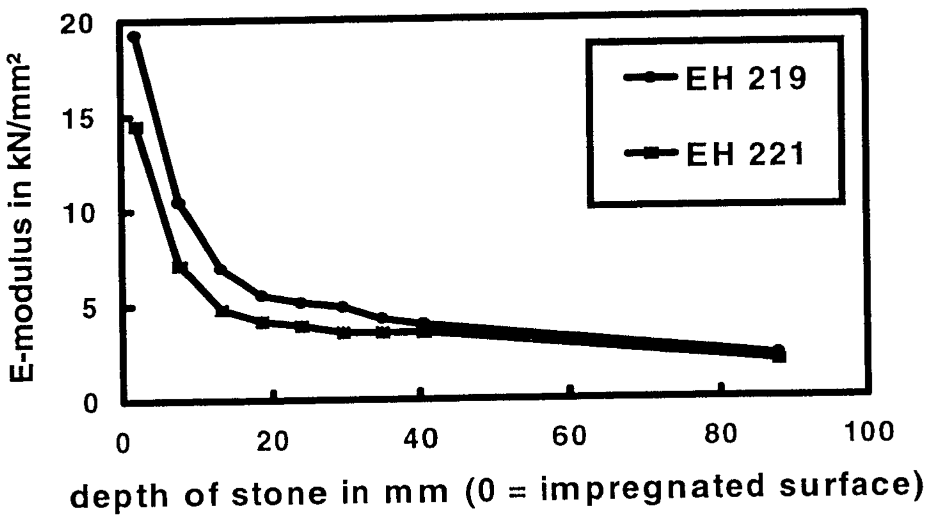


Figure 5: Modulus of elasticity of Ebenheider Sandstone, treated with the agents No.219 and 221

5 Conclusion

A stone protecting agent was improved by introducing new modified isocyanate monomers. Treated natural stones show a high impregnation depth of the agent as well as good water repellent properties. The stone is strengthened and the water vapour diffusion is lowered to a low extent. A main aspect of the new development was the consideration of working safety aspects. The toxicity could be kept low by the use of the new monomer types.

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