WATER-THINNABLE SILICONE IMPREGNATING AGENTS FOR MASONRY PROTECTION

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INTRODUCTION

Silicone impregnating agents have been used successfully for more than 35 years to protect absorbent building materials against moisture. Masonry impregnation not only prevents the substrate from absorbing water but also provides protection against a variety of other damage caused by the constant exposure of the building material to moisture, e.g. efflorescence of salts, leaching of lime, frost damage and infestation with moulds, algae and mosses.

Water-repellent silicone impregnating agents are easy to use and highly effective in masonry protection. They can be applied on many different substrates such as clay brick, concrete, calcium silicate brick, plaster and all types of natural stone.

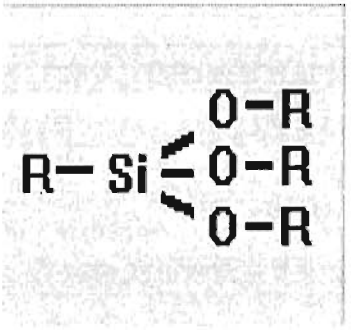
The key requirements made of such impregnating agents are shown below:

- good water-repellent properties
- universal application
- good alkali resistance
- good penetration properties
- unaltered appearance of the substrate
- excellent water vapour permeability
- durability

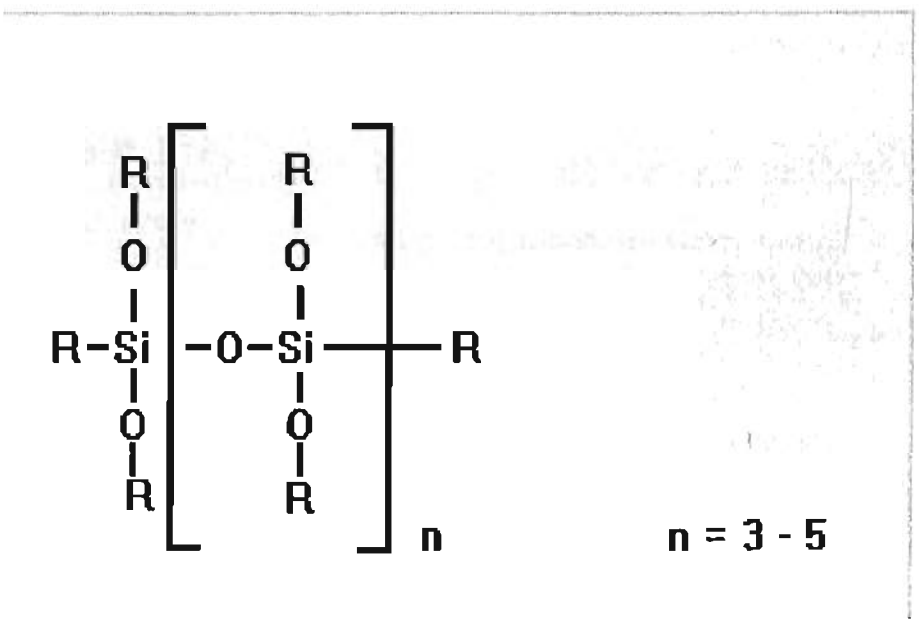
1 STATE OF THE ART

The active substances in the impregnating agents are organic silicon compounds with different degrees of condensation. The ready-to-use solutions contain large amounts of organic solvents. Because of the widespread use of reactive condensation systems, there is an associated cleavage of alcohols.

Silanes, siloxanes and, to a lesser extent, silicone resins (polysiloxanes) can be used as active substances. The silanes most commonly used in masonry protection applications are alkyl alkoxysilanes which have the following formula:



The O-R groups may be either methoxy or ethoxy groups. These reactive groups are necessary for the formation of crosslinked molecules (polysiloxanes) on the surfaces of the pores or capillaries of the building material. The product of this reaction is methanol or ethanol. Silanes are used as pure active substances or in solution, e.g. 40 %. Siloxanes are precondensed silanes with the following general formula:



The content of reactive groups is lower than in silanes. Nevertheless, alcohols are also formed during the condensation reaction which produces polysiloxane.

Silicone resins (polysiloxanes) are non-reactive substances which dry by physical mechanisms and therefore produce no cleavage products.

Siloxanes and silicone resins are used in highly diluted solutions. The ready-to-use impregnating agents have a high organic solvent content - around 90 %. The solvents normally used are hydrocarbon compounds such as white spirit, isoparaffins, possibly mixed with alcohols, esters and ketones.

The alkyl groups on the silicon, shown by the R in the formula, are mainly methyl groups. For applications on fresh concrete, plaster, mortar and other alkaline substrates, it has been found that products containing higher alkyl groups such

as propyl, butyl and octyl perform well. More highly alkylated silicone impregnating agents have greater resistance to alkalis than comparable methyl compounds. In practice, it is sufficient to substitute some of the methyl with other alkyl groups. Table 1 provides an overview of the properties of the active substances used.

TABLE 1
Overview of the active substances.

Overview of the active substances

Properties	Silane	Siloxane	Silicone resin
Chemical structure	Monomer	Oligomer	Polymer
Molecular weight [g/mole]	≤ 300	700 - 1,000	> 3,000
Application concentration [% by wt.]	40 - 100	8 - 12	5 - 6
Alcohol cleavage from active substance [% by wt.]	Approx. 50	Approx. 20	None
Penetration	Very good	Good	Poor
Solvents used in preparing ready-to-use solutions	Alcohols	Aromatic and aliphatic hydrocarbons, iso-paraffins, alcohols	Aromatic and aliphatic hydrocarbons, alcohols, esters, ketones

2 NEW WATER-THINNABLE SILICONE IMPREGNATING AGENTS

2.1 CHRONOLOGY

Bayer AG began developing new water-thinnable products more than ten years ago. In 1987, a Trial Product based on an emulsified alkyl alkoxysilane was introduced. After market trials and acceptance by our customers, the first commercial product in a new generation of masonry protection agents was launched under the name Baysilone Impregnating Emulsion LD in 1990. The focus of applications for this product are large-pored building materials such as clay brick products and plaster. Efforts to improve product quality yielded a further Trial Product, AI 3462, in 1994.

The sequence described above shows clearly that the development and introduction of new technologies requires considerable investment in terms of both time and money. It goes without saying that the process is very gradual since experience of the products must be gained systematically.

2.2 TECHNOLOGY AND RAW MATERIALS

The organic silicon compounds described in Section 1 also form the basis for water-thinnable systems. The focus is on raw materials of low molecular weight such as siloxanes and silanes.

A highly effective emulsification process disperses the active substances finely in the aqueous phase, yielding emulsions which are miscible with water. The addition of stabilisers prevents undesirable reactions of the active substances in the aqueous medium, thus ensuring storage stability. There is no need to use organic solvents in the formulation of ready-to-use solutions. Because of the reactive raw materials used, small amounts of alcohol are still formed as the result of cleavage.

2.3 PROPERTIES

The requirements made of impregnating agents are fully satisfied by existing state-of-the-art products. Further optimisation of the emulsification process and greater experience in the selection of the active substances mean that there is now no difference between the properties of water-thinnable and solvent-borne masonry protection agents. The poor penetration properties of the first-generation products have been improved considerably. The use of only highly alkylated raw materials allows universal application, both on neutral and fresh cement- or lime-bound building materials.

Figure 1 compares the capillary water absorption of the new emulsions on various building materials. The improved results in reducing capillary water absorption obtained using TP AI 3462 are largely due to the improvement of the penetration properties.

This has expanded the potential applications to include more compact and less absorbent building materials such as concrete and cement-based mortars.

Comparison of TP AI 3462 with conventional solvent-borne silicone impregnating agents confirms these excellent results.

Tables 2 to 6 show the products tested and the results of the comparison of their effectiveness as impregnating agents on four different building materials (clay brick, calcium silicate brick, cement-based mortar and lime-cement plaster). This comparison also shows clearly the high level of performance now yielded by water-thinnable silicone impregnating agents.

FIG.1

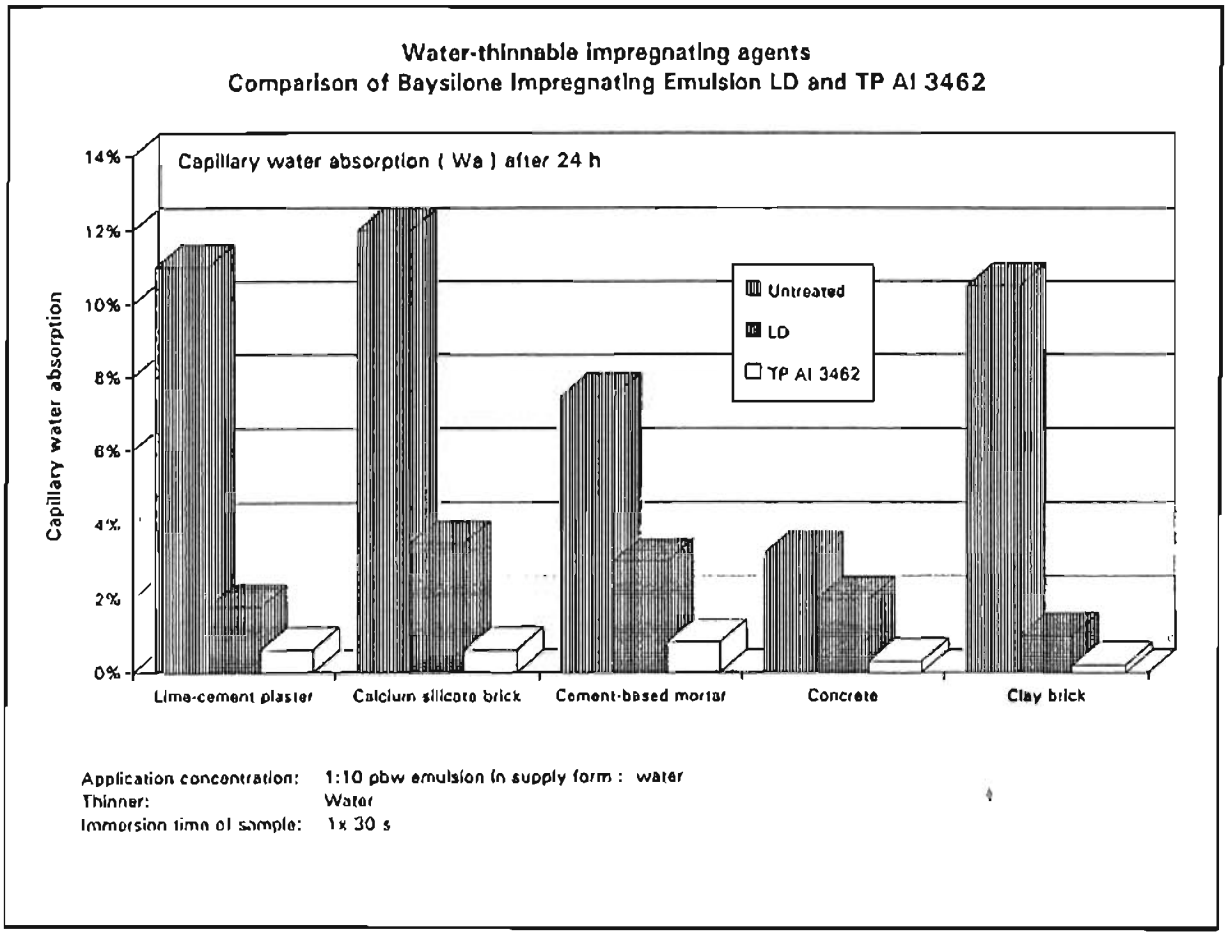


TABLE 2

Baysilone Impregnating Agents

Comparison of solvent-borne products and a water-thinnable emulsion

Product	Type	Form supplied (% by wt.)	Dilution (pbw)	Concentration (% by wt.)	Thinner
LV-N	Silicone resin	50	1 : 9	5	White spirit
LO-N	Alkoxysiloxane	100	1 : 12	8	White spirit
TP AI 3462	Silane/siloxane emulsion	60	1 : 7 - 1 : 10	7.5 / 5.5	Water

TABLE 3

Baysilone Impregnating Agents

Effectiveness on clay brick

Product	Concentration (% by wt.)	Amounts used (g/m²)	Amounts used (ml/m²)	Penetration (mm)	Pearl-off effect*	Capillary water absorption (% by wt.) 2 h	6 h	24 h	Immersion in 0.1 n KOH Increase in weight (%) 1 day	2 days	7 days
LV-N	5	1,070	1,340	15	+	0.1	0.1	0.2	0.5	0.6	0.7
LO-N	8	1,070	1,340	20	+-	0.1	0.1	0.2	0.6	0.6	0.6
TP AI 3462	7.5	1,080	1,080	11	-	0.1	0.2	0.3	0.5	0.6	0.6
TP AI 3462	5.5	1,120	1,120	10	-	0.1	0.1	0.3	0.6	0.6	0.6
Untreated	-	-	-	-	-	12.8	13.0	13.6	-	-	-

* + = good
+- = poor
- = none

TABLE 4

Baysilone Impregnating Agents

Effectiveness on calcium silicate brick

Product	Concentration (% by wt.)	Amounts used (g/m²)	Amounts used (ml/m²)	Penetration (mm)	Pearl-off effect*	Capillary water absorption (% by wt.) 2 h	6 h	24 h	Immersion in 0.1 n KOH Increase in weight (%) 1 day	2 days	7 days
LV-N	5	230	290	0.5 - 1	+	0.2	0.4	0.9	0.9	1.4	2.2
LO-N	8	210	260	2 - 3	+-	0.2	0.3	0.6	0.7	0.8	1.3
TP AI 3462	7.5	280	280	1 - 2	+-	0.2	0.4	0.6	0.6	0.8	1.1
TP AI 3462	5.5	300	300	1	+-	0.2	0.4	0.7	0.7	0.9	1.3
Untreated	-	-	-	-	-	10.5	10.5	10.5	-	-	-

* + = good
+- = poor
- = none

TABLE 5

Baysilone Impregnating Agents

Effectiveness on cement-based mortar

Product	Concentration (% by wt.)	Amounts used (g/m²)	Amounts used (ml/m²)	Penetration (mm)	Pearl-off effect*	Capillary water absorption (% by wt.) 2 h	6 h	24 h	Immersion in 0.1 n KOH Increase in weight (%) 1 day	2 days	7 days
LV-N	5	180	230	0.5 - 1	+-	0.3	0.5	1.1	3.3	5.8	5.9
LO-N	8	160	200	2	+-	0.2	0.5	0.9	0.8	1.0	1.3
TP AI 3462	7.5	220	220	1 - 1.5	-	0.3	0.4	0.8	0.7	0.9	1.3
TP AI 3462	5.5	200	200	1	-	0.4	0.5	0.9	0.8	1.0	1.4
Untreated	-	-	-	-	-	6.1	6.1	6.1	-	-	-

* + = good
+- = poor
- = none

TABLE 6

Baysilone Impregnating Agents

Effectiveness on lime-cement plaster

Product	Concentration (% by wt.)	Amounts used (g/m²)	Amounts used (ml/m²)	Penetration (mm)	Pearl-off effect*	Capillary water absorption (% by wt.) 2 h	6 h	24 h	Immersion in 0.1 n KOH Increase in weight (%) 1 day	2 days	7 days
LV-N	5	500	630	3 - 4	+	0.3	0.4	0.7	0.7	0.7	1.0
LO-N	8	470	590	4 - 5	+-	0.3	0.4	0.7	0.7	0.7	0.9
TP AI 3462	7.5	550	550	2 - 3	-	0.4	0.4	0.8	0.8	0.9	1.0
TP AI 3462	5.5	490	490	2 - 3	-	0.4	0.6	0.9	0.8	0.9	1.1
Untreated	-	-	-	-	-	9.4	9.5	9.7	-	-	-

* + = good
+- = poor
- = none

The following results are worth particular mention.

- Good penetration properties on all four types of building material. In some cases, the values are higher than for silicone resin.

- Comparable impregnating agent consumption for both water-thinnable and solvent-borne solutions.

- Very good reduction of capillary water absorption.

- Excellent resistance to alkalis.

On the basis of these test results, the many different applications shown in Table 7 are possible.

The application of masonry impregnating agents is weather-dependent. Good penetration properties and long-term protection can only be achieved on dry substrates.

It is reasonable to conclude that moist substrates could also be treated effectively using water-thinnable systems.

In an effort to substantiate this conclusion, laboratory trials were carried in which building materials with a high moisture content were impregnated.

Table 8 shows the results of tests using clay brick and calcium silicate brick with a water content of 70 % by weight, calculated on the dry building materials. The absorption of the impregnating agent was determined. The values shown represent the mean of 10 tests. Because of the extreme deviation, the highest and lowest values were not included.

TABLE 7

Baysilone Impregnating Agents for mineral building materials

Baysilone Impregnating Agent	LF	LO-N	LV-N	LD	TP AI 3462	SK
Recommended dilution						
Parts by vol.	1 : 6 - 7	1 : 15 - 16	1 : 11 - 12	1 : 6 - 8	1 : 10	1 : 10
Parts by wt.	1 : 5	1 : 12	1 : 9	1 : 6 - 8	1 : 10	1 : 8
Concrete	+	+	+		+	
Clay roof tiles				+ *	+	+ *
Exterior plaster	+	+	+	+	+	
Gas concrete	+	+	+	+	+	
Gypsum products						+
Calcium silicate brick	+	+		+	+	
Unglazed engineering brick	+	+	+	+	+	
Light concrete	+	+	+	+	+	
Natural stone	+	+	+		+	
Facing brick	+	+	+	+	+	
Cement-based mortar	+	+			+	
Clay brick	+	+	+	+	+	

= solvent-borne

= water-thinnable

* In industrial applications, e.g. using the dipping process, the product must be diluted further, e.g.

LD 1 : 100 - 150 parts by vol.

SK 1 : 60 - 100 parts by vol.

TABLE 8

Absorption of TP AI 3462 diluted 1 : 9 (pbw) with water

Calcium silicate brick		Clay brick	
Dry	Moist	Dry	Moist
300 g/m²	150 g/m²	1,100 g/m²	600 g/m²

A further trial was carried out using cement-based mortar samples with a water content of 78 % by weight and three different dilutions of TP AI 3462. The results are shown in Table 9.

TABLE 9

Absorption of different dilutions of TP AI 3462

	Cement-based mortar	
Dilution	Dry	Moist
1 : 3 pbw	240 g/m²	130 g/m²
1 : 5 pbw	340 g/m²	120 g/m²
1 : 7 pbw	340 g/m²	120 g/m²

The results shown in Tables 8 and 9 reveal that moist building materials absorb considerably less impregnating agent than dry building materials. The reduction in absorption is some 50 to 65 %, depending on the type of building material. Tests of the penetration properties on the moist samples also yields a reduction in values of up to one half.

However, it is interesting to note that assessing the samples at different stages of drying reveals an improvement in the penetration of TP AI 3462. This is probably attributable to a "creeping" of the low-molecular-weight components of the system.

Nevertheless, it is generally inadvisable to apply an impregnating agent on very moist substrates. As has already been stated, the optimum effectiveness of silicone impregnating agents is only guaranteed when they are applied on dry building materials.

Further trials have been carried out to investigate the water vapour diffusion of impregnated building materials. Our own trials and those carried out by an independent test institute show that the emulsions, like the solvent-borne impregnating agents, have no significant effect on the diffusion properties.

2.4 PRACTICAL EXPERIENCE

In October 1992, trials were carried out using a laboratory product which, with a few minor variations, was the same as TP AI 3462.

45 m^2 of a west-facing engineering brick wall on an industrial building were sprayed with the impregnating agent. The problem here was the very high water absorption of the pointing mortar. The impregnating agent used was a mixture of 1 part by weight emulsion and 7 parts by weight water. Some 480 ml of the preparation were required per square metre. The temperature on the day of application was between 10 and 12°C and it rained the following day.

Four weeks after application of the impregnating agent, water absorption tests were carried out using Karstens test tubes. These tests showed that the impregnating agent was performing perfectly.

After three years' weathering, the impregnation is still in perfect condition, as shown by the water penetration tests carried out (see Table 10).

TABLE 10

Water absorption tests using Karstens test tubes (10 cm water column) after 3 years' weathering

	Engineering brick	
	Untreated	Impregnated
15 min	0.3 cm^3	0 cm^3
30 min	0.7 cm^3	0 cm^3
45 min	0.9 cm^3	0 cm^3
60 min	1.2 cm^3	0 cm^3

	Pointing mortar	
	Untreated	Impregnated
5 min	6.5 cm^3	0 cm^3
10 min	12.5 cm^3	---
15 min	17.0 cm^3	0 cm^3
20 min	22.0 cm^3	---
30 min	---	0 cm^3
45 min	---	0 cm^3
60 min	---	0.1 cm^3

3 OUTLOOK FOR THE FUTURE

The tightening of legislative measures and an increase in the environmental awareness of the public will make the use of solvent-borne masonry impregnating agents increasingly difficult in the future. However, from the point of view of the manufacturers of silicones for masonry protection applications, there are no grounds for concern.

Bayer AG has developed water-thinnable silicone emulsions which require no organic solvents for application. The second generation of these new products is technically equivalent to the existing conventional systems and represents a solvent-free alternative.

Practical experience with the new products is not yet as extensive as with the tried-and-tested solvent-borne systems but the signs are very encouraging. The similarity of the active substances used and the equivalent performance in comparative tests with solvent-borne impregnating agents confirms the high degree of effectiveness of the new water-thinnable silicone impregnating agents for masonry protection.

4 SUMMARY

Water-thinnable silicone impregnating agents have been developed as technically comparable alternatives to the widely used solvent-borne products such as siloxanes and silicone resins.

Baysilone Impregnating Emulsion TP AI 3462 satisfies industry requirements in terms of penetration properties, water repellency and water vapour permeability.

High resistance to alkalis allows universal application on all porous building materials such as concrete, cement-based mortar, calcium silicate brick, clay brick, rendering and natural stone.

Trials have shown that dry substrates absorb comparable amounts of water-thinnable impregnating agents and solutions of solvent-borne systems. Impregnating agent absorption and penetration are reduced on moist substrates. A test surface treated about three years ago with the new water-thinnable impregnating agent has excellent water-repellent properties after weathering in an industrial atmosphere.