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A New Approach for Self-Cleaning Silicone-based Facade Coatings

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Abstract

Since being introduced in 1963, silicone resin emulsion paint (SREP) has developed into one of the most modern facade coating systems. While specific formulations and raw materials have changed in the last 42 years, the long-lasting performance properties resulting from the unique combination of water repellency, vapour permeability, low VOC and the silicon-resin based structure have remained consistent. A general characteristic of mineral construction materials is their porous structure. Because these structures readily absorb water, exterior walls are quickly discolored or damaged by rain. This drawback makes facade protection essential. With the growing use of insulating masonry and lightweight plasters, a water-vapour permeable finish is a key requirement, since, in a well-protected facade, any absorbed moisture must be able to escape to the atmosphere. The masonry protection features must also last as long as possible. Finally, a facade coating that protects the outer wall against water or environmental or chemical attack must also have an attractive appearance. Under certain circumstances or certain local environmental conditions it may be required to install a facade coating with furthermost reduced dirt pick-up. As the most recent development in this area the properties of tailor-made silicone-resin emulsion paints with convincing self-cleaning properties will be presented.

1 Introduction

Whether the construction industry is restoring, modernizing or erecting new buildings, it is fighting a constant battle against decline, both financial and cultural.

Financial decline in the sense that research has shown that buildings depreciate most in value within five years of completion.

Cultural decline in as far as we neglect our heritage when we allow our most precious monuments and historic buildings to go to rack and ruin.

Water has always been and remains the most common source of serious damage in ancient and modern buildings because it transports harmful substances and microorganisms into the very heart of the structure, where they can wreak havoc. And yet, there are effective measures available that will protect against moisture decay.

This paper will give an overview about chemistry and the major features of silicone resin emulsion paints (SREP®) (SREP® is a registered trademark of Wacker-Chemie GmbH) and an example for a consequent ongoing development of this masonry protection system.

2 Capillary water absorption

Since building materials can absorb water only through their pores, porosity holds the key to the whole problem of water uptake. When these hydrophilic building materials come into contact with water, the amount absorbed depends on their porosity and pore size distribution. Furthermore, if the pores act as passageways for water and any concomitant aggressive substances, the result is damage in various forms, including:

- Penetration of moisture through the wall
- Cracks due to swelling and shrinkage
- Damage caused by frost and de-icing salt
- Efflorescence and salt damage caused by hydration and crystallization
- Lime leaching
- Rust stains
- Dirt pick-up
- Attack by fungi, moss, lichen and algae
- Chemical corrosion, e.g. binder transformation caused by acidic gases (SO_2NO_X)
- Impairment of the thermal insulation property
- Destruction of concrete due to corrosion of reinforcement

A substantial reduction of capillary water absorption by silicone-based materials is known and used in practice since the early 1950ies. Those products are used as hydrophobizing mass- or surface impregnants or as ingredients of coating systems (additives or binders). In this paper only the coatings-part will be concerned.

3 Chemistry and properties of silicone resins

3.1 Siloxanes

The term siloxane can lead to confusion since, strictly speaking, it refers to the Si-O-Si linkage, which is characteristic for all silicone-based products.

However, in the construction industry, and therefore in this paper, the term "siloxane" is used to denote alkylalkoxysiloxane. The expression arose because between three and six monomeric T unit alkylalkoxysilane molecules undergo a condensation reaction involving the formation of siloxane bonds to produce oligomeric alkylalkoxysiloxane molecules (i.e. with few units). Depending on the particular silane raw material used, the siloxanes produced incorporate either methanol or ethanol and either long (octyl) or short (methyl) alkyl groups. Siloxanes are typically transparent, mobile, but non-volatile liquids. E.g. a methylsiloxane, comprising six T units, has an alcohol content of only 30 to 40 % by weight.

The remaining alcohol groups undergo a condensation reaction with available substrate groups (usually Si-OH), forming silanol, or react with one another, to further crosslink the silicone resin into a silicone resin network (Fig. 1).

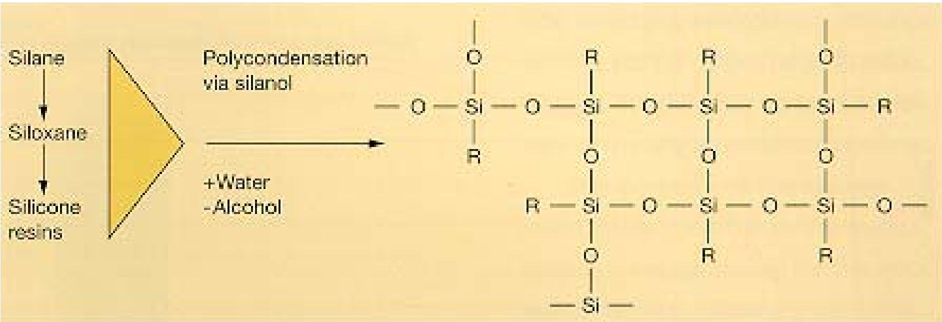

Figure 1: Schematic deveolpment of a silicone resin

Figure 2: Silicone resin flakes

3.2 Silicone resins

Silicone resins are high-molecular, three-dimensionally crosslinked compounds, based – like quartz – on a silicon/oxygen skeleton. Unlike quartz, however, every fourth oxygen atom of a silicone resin is replaced by an organic group R. It can therefore be described as an organically modified quartz structure. All silicone resins consist of silicon T (= "trifunctional") sub-units. Chemically speaking, silicone resins form an intermediate class between purely inorganic and purely organic substances (Fig.2).

Silicone resins consist of 30 to 80 silicon T-units with molecular weights of 2000 to 6000 – which is very low compared to organic resins. The density of the resins varies from 1.1 to 1.2 g/cm³ as a function of the resin blend. They also contain 2 to 4 % of residual alcohol (ethanol). Methyl silicone resins have the most inorganic character of all silicone resins. When fully reacted, they contain only 11 wt % of thermally decomposable organic residues. Only pure silicon dioxide remains.

Methyl silicone resins dry from organic solution or emulsion to form a non-tacky film (physical drying), which is itself fully water-repellent.

4 Silicone resin emulsion paint

4.1 Principle and theory behind silicone resin emulsion paint (SREP®)

The porosity of mineral-based masonry materials makes it necessary to protect facades with surface coatings. The most important technical property for a good wall coating is that it protects against water and other environmental and weather-related influences. The coating must exhibit good water-vapour permeability – while meeting specifications for low water absorption – to ensure that damp facades dry out quickly. Most of all, however, the coating must be very durable and must resist dirt pick-up. The usually most suitable facade-coating systems for meeting these structural and technical requirements are based on non-pore-sealing silicone resin emulsion paints because they combine the benefits of mineral and polymer-dispersion-bound coatings. The silicone resin binder provides the mineral-like to the silicone resin emulsion paint. Silicone resin tends to be inorganic in nature because of its three-dimensionally crosslinked modified-quartz structure.

4.2 Model of how silicone resin emulsion paints work

For an understanding of how SREP® works, it is vital to know how the binders are distributed and how the silicone resin network is formed in the paint microstructure. Fig. 3 illustrates the microstructure of a silicone resin emulsion paint. The differences in the working principles of an elastomeric, film-forming emulsion paint (I) and a silicone resin emulsion paint (II) are compared below.

In highly elastomeric emulsion paints with a low PVC (e.g. < 35 %), the binder not only covers all of the fillers and pigments, but surplus fills all of the voids. Although this kind of paint, which is formulated below the critical PVC and whose coating effect derives from the formation of a film that clogs or seals the pores, is extremely effective at preventing water absorption, but it prevents the transmission of water vapour. Consequently, because diffusion cannot occur, moisture coming from within the masonry may lead to the formation of blisters, and ultimately flaking of the paint.

In a silicone resin emulsion paint with a high PVC (e.g. > 60 %), the binder is distributed such that the pores are coated but not sealed, with some of the polymer dispersion replaced by silicone resin binder. Because there is less polymer binder, there is not enough of it to fill the voids between filler particles and so the interstices are filled with air. The polymer binder acts as a bridge by binding individual filler and pigment particles together but does not seal pores on an extensive scale. For this open-pore structure to exhibit good water repellency, the exposed mineral fillers/pigments must be almost completely enveloped by the silicone resin. In addition to being very good at rendering the pores water repellent, silicone resin has a strong affinity for mineral substrates, a fact which implies that the pores are also reinforced and this is a distinguishing feature of the binder character of silicone resin.

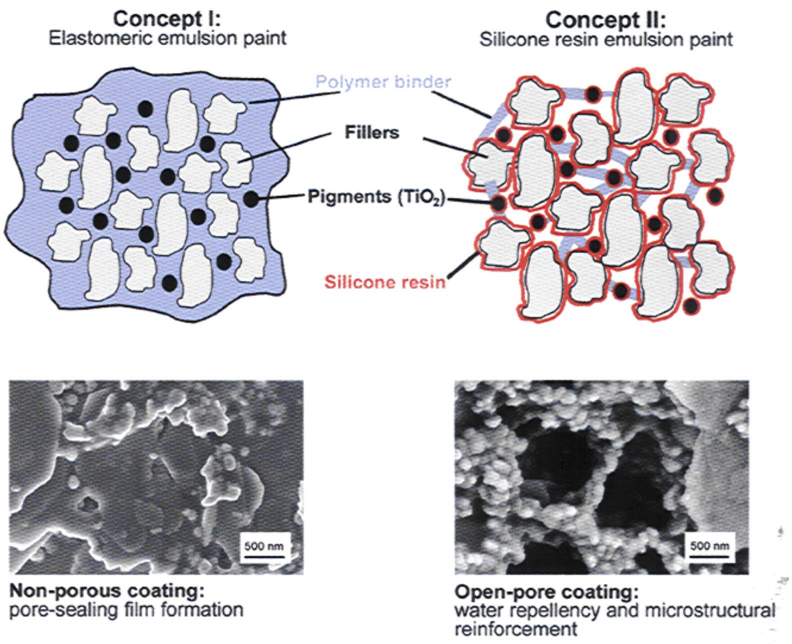

Figure 3: Comparison between film-formig coating and SREP®

4.3 The features of silicone resin emulsion paints

The features of SREP® have already been described several times (e.g. [1]-[4]), also approaches with added values are reported [5]. The most important features can be – aside the art of formulating a high performance paint – reflected to the silicone resins´ properties, even if there are only 5 % actives available in the formulation listed above (Tab. 1):

- Water repellency

…is achieved by the organic group (methyl group) of the silicon resins. The inorganic portion of the silicone resin has a strong affinity to the filler and the inorganic pigments. The hydrophobic groups project into the capillaries and pores, rendering them water-repellent.

- Water vapour permeability

…is generated by the pore-lining behavior of the silicone resins. Extremely thin resin films are generated inside the capillaries and on the surface of fillers and pigments silicone resins are the most water-vapour permeable form of silicones. This is the result of their skeleton, 80 % of which is inorganic silicon and oxygen.

Table 1: Exemplary guiding formulation for a SREP®

typical formulation	parts by weight
Water	305
Dispersing aid/wetting agent	4
Thickener	5
Sodium hydroxide, 10 % conc.	1
Defoamer	3
Film-forming aids	10
TiO_2	120
Fillers	335
Silicone resin emulsion	100
Silicone water repellent additive	10
Preservative	12
Polymer emulsion	95
Total	1 000

- Weathering and temperature resistance

Silicone resins are resistant to the ultraviolet and infrared components of sunlight. They show a much better heat-resistance than most organic polymers. It can be shown by thermogravimetric measurements that the methyl groups start to split off at temperatures of ca. 300 °C. The weight loss in this case is in the range of ca. 20 %, pure SiO_2 remains.

- Paintability

Silicone resins are the only class of silicone products that can be painted. This distinguishes them from silicone fluids and silicone elastomers. Silicone elastomers can be made paintable by modification with silicone resin products.

- Mineral appearance

The cause of the mineral appearance is the silicone resin network, which resembles the structure of quartz and waterglass. It derives from the silicone resin main binder.

- Pigment-binding power

Unlike water-repellent additives based on silicone fluids, silicone resin emulsion paints show extremely high abrasion resistance, especially after weathering. This is related to the inorganic character of the silicone resin structure, which also explains why the pigment-binding power and chalking behaviour resemble those of waterglass. The silicone resin binder acts as a water repellent and reinforcing agent in the pores, comparable to the steel reinforcement in reinforced concrete.

- Longevity

It can be shown that the inherent properties of silicone resin emulsion paints and plasters can make them more durable than purely emulsion-bound coatings and they thus offer superior cost effectiveness. Life-cycles of more than 25 years for a SREP®-coating are reported [6, 7].

- Low dirt pick-up

Paints based on solid silicone resins usually show almost no dirt pick-up in practical tests extending over several years. Special conditions may require a different approach for an additionally reduced dirt pick-up, or eventually self-cleaning properties.

- Microbial attack

Because the surfaces of silicone resin emulsion paints and plasters are highly water-repellent – thanks to the permanently-incorporated silicone resin – the coating is drier for a longer period of the year on average. This reduces the opportunity for colonization by microbes such as algae or fungi.

5 Self-cleaning facades

5.1 Remarks

There are several approaches to create facade coatings with extremely little to no dirt pick up. In most cases and e.g. in central Europe the usual SREP®-technolgy provides with a satisfying long-term cleanness. Dependent on the climatical and air pollution situation this situation may change and additional features may be required.

5.2 Principal approaches

One theoretical approach is the addition of fluoro polymers as water- and oil-repellent additives to paint systems. The self-cleaning effect is usually only required on the surface of a coating, while an additive is normally equally distributed within the whole coating. As a certain minimum amount of active (fluoro) ingredient must be generated close to the surface to achieve a sustainable effect, the amount of the additive in the whole system must be relatively high. The high market prices for fluoro-based products practically limit their application in this field.

While the use of fluoro-compounds has not led to wide-spread recognition in the market, other concepts have reached awareness and are discussed as possible solutions. A look into the nature showed that leafs, plants and vegetables in many cases have a surprisingly low tendency for dirt pick-up und soiling. An analysis of the scientific reasons for this behavior enabled coating specialists to transfer this concept into a paint. The first "Lotus-effect®" paint has been launched in 1999 and combines hydrophobicity and a special microstructure on the surface of a coating. The effect of such a "Lotus-effect®" paint finally can be seen in the low adhesion of dirt particles to the coating surface.

The concept which will be discussed in this paper is the concept of photo-active ingredients in a hydrophobic paint. Some inorganic oxides or sulfides (Anatas-TiO_2, ZnS) are known to have photocatalytic characteristics. Especially TiO_2 is already used in a variety of applications as there are

- NO_x decomposition
- Water Treatment
- Deodorization
- Anti-Bacteria Treatment
- Dirtiness Prevention.

The effectiveness of such a photoactive substance is based on the generation of OH-radicals which react with readily available other radicals (NO_x) or hydrogen atoms of organic origin. The latter mechanism leads to a step-by-step decomposition of organic material finally to carbon dioxide and water (Fig. 4).

Especially the principal feature of dirt prevention is the major focus and target if TiO_2 is used as ingredient of a facade coating. In case of a silicone resin emulsion paint the inherent hydrophobic effect can so be combined with photocatalytic active ingredients.

5.3 Photocatalytic silicone resin emulsion paint

From the detailed formulations (Table 2) it can be seen that a lot of the paint ingredients contain C-H-bonds, which can be principally affected by OH-radical-induced degradation, but especially close to the surface it is finally only a question of probability and dirt composition, which organic molecule will be attacked first.

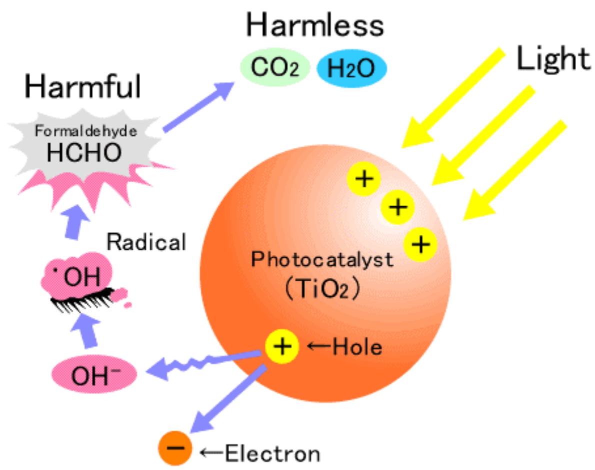

Figure 4: Schematic view of TiO_2 (Anatas) as photocatalyst

In a test series a SREP® guiding formulation (Table 1) has been equipped with 3, 5 and 7 % of a TiO_2 photocatalyst and several parameters have been compared after 12 month outdoor exposure (Burghausen, Germany).
It is found from the outdoor exposure experiments that the water-absorption (w24-value) and water-vapour-permeability (sd-value) levels of anatas-modified paints do not differ significantly from a common formulation.

The major features of the anatas additive is obvious as soon as the colour difference (L, a, b-system) and the dirt collection index Dc are taken into account.

The paints equiped with photocatalyst show a significantly less colour change and less dirt pick-up. Even at the lower doasage level (3 %) the effect is already convincing, so that probably even lower amounts may lead to sufficient results. It is interesting that the photocatalyst systems seem to have the ability to recover. This can be explained by a rain induced dirt removal.

The results of the semi-quantitative chalking test indicate that there is indeed a slightly higher chalking tendency for the photocatalytic paints, independent from the dosage. This effect may be explained by the slight degradation of organic ingredients of the paint system, especially the organic binder, which is mainly responsible for the fixation of the single ingredients (see Fig. 3). This behavior leads to an effect which is already known as "noble-chalking". In case of paints which had been formulated with only silicone resin emulsions as single binder, the binder capacity had been not sufficient, so that a chalking occurred similar to a lime-wash- or silicate-paint

Table 2: Tested SREP® formulations with photocatalytic TiO_2

Nr.	raw material	UV 100-3	UV 100-4	UV 100-5
		3 % UV 100 BS 54	**5 % UV 100 BS 54**	**7 % UV 100 BS 54**
1	deionised water	300,0	300,0	300,0
2	Lopon 890	2,0	2,0	2,0
3	Calgon N	2,0	2,0	2,0
4	Acticide MBS	2,0	2,0	2,0
5	Acticide MKA	10,0	10,0	10,0
6	Walocell XM 20000 PV	3,0	3,0	3,0
7	WACKER Antifoam S 860	3,0	3,0	3,0
8	Lusolvan FBH	10,0	10,0	10,0
9	Kronos 2190	120,0	120,0	120,0
10	Omyacarb 5 GU	185,0	165,0	145,0
11	Plastorit 000	80,0	80,0	80,0
12	Steopac	40,0	40,0	40,0
13	OpTiMat 2550	12,0	12,0	12,0
14	**Hombikat UV 100, Fa. Sachtleben**	30,0	50,0	70,0
15	**SILRES BS 54**	93,0	93,0	93,0
16	Sodium hydroxide, 10%	1,0	1,0	1,0
17	Vinnapas SAF 54 W	95,0	95,0	95,0
18	Tafigel PUR 40	2,0	2,0	2,0
	sum	990	990	990

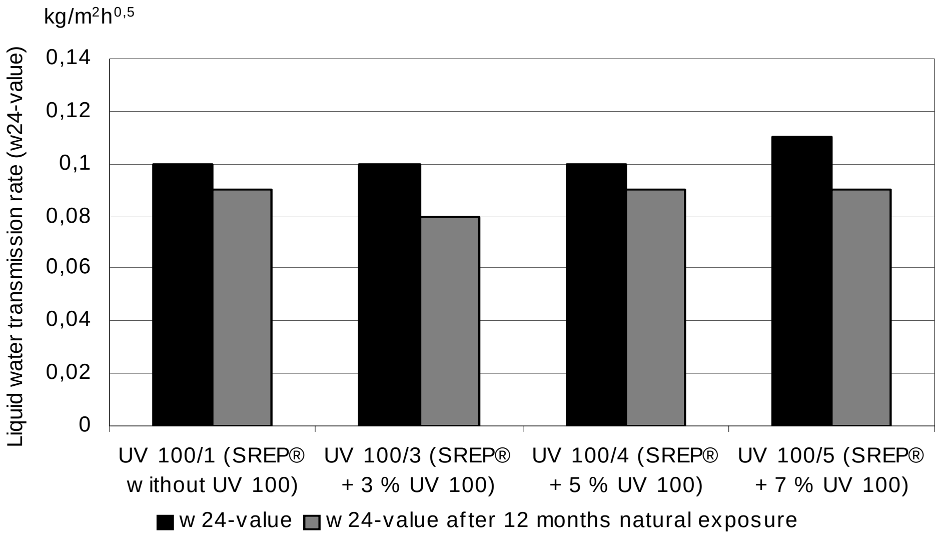

Figure 5: Liquid water transmission rate (w24-value) in $kg/m^2h^{0,5}$

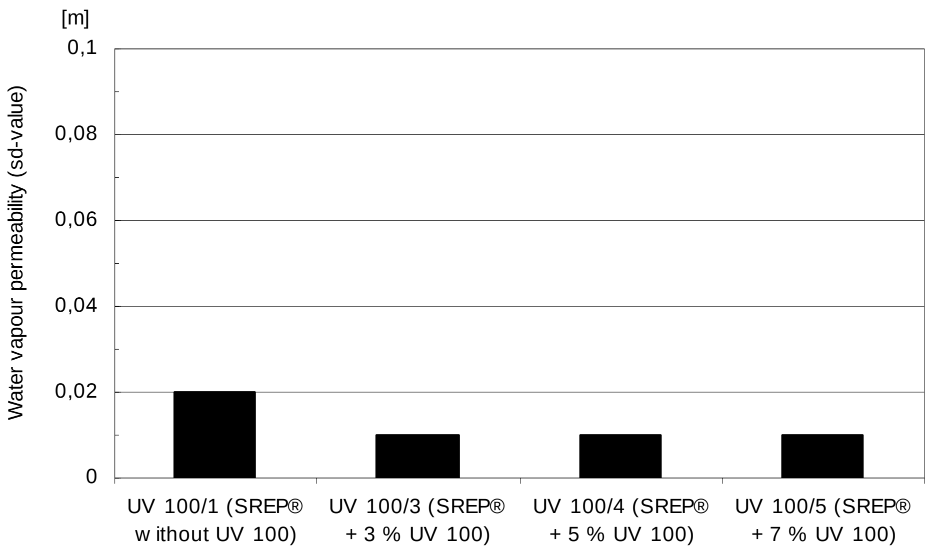

Figure 6: Water vapour permeability (sd-value)

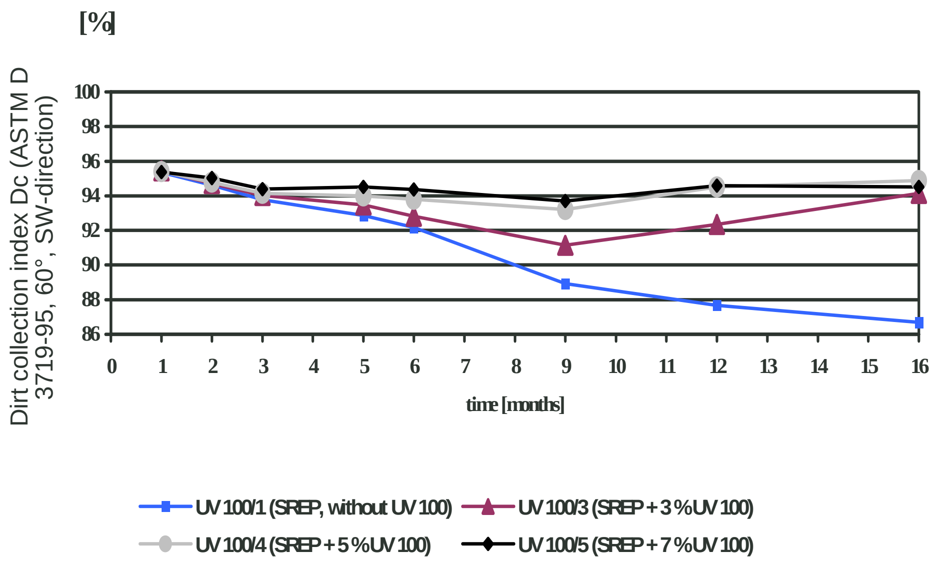

Figure 7: Dirt collection index Dc (ASTM D 3719-95, 60°, SW-direction)

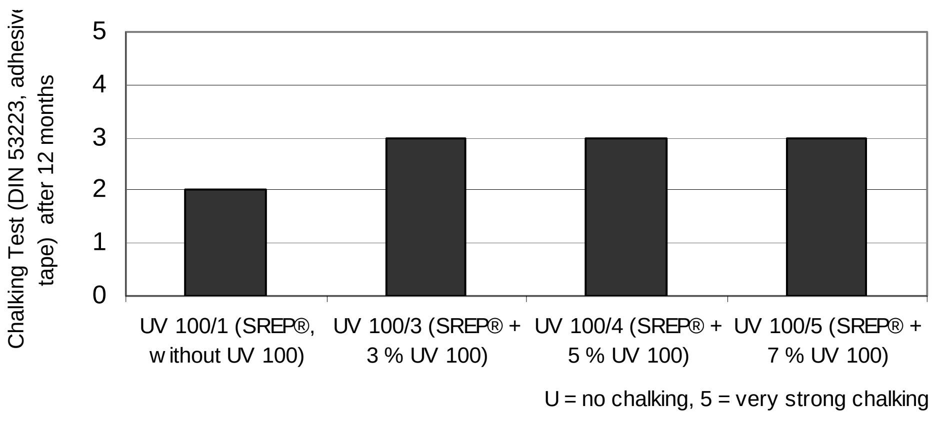

Figure 8: Chalking Test (DIN 53223, adhesive tape) after 12 months

with the difference that the fresh surface contained a lot of silicone resin and therefore always showed a good hydrophobicity.

In case of the TiO_2-modified paints there seems to be a similar behavior as the water-repellency of the surface after 12 respectively 16 months is still in a good shape. Higher contents of photocatalyst lead to more hydrophilic surfaces.

Parallel tests from an outdoor exposure area in Shanghai indicate an identical behavior of a photocatalyst-modified SREP® even under the different climatical and pollution situation there.

6 Conclusion

The porous surface structure of hydrophilic mineral wall construction material makes it essential to apply protective exterior coatings. Silicone resin emulsion paints formulated above the critical PVC meet the demand for maximum water vapour permeability combined with a very low water absorption coefficient.

If necessary it is possible to generate Silicone Resin Emulsion Paints with self cleaning properties by adding a photocatalyst to the formulation. The physical properties of the SREP® system remain unchanged, while the cleanliness will be additionally improved.

The practical benefits of silicone resin emulsion paint can only be observed by examining the exteriors of buildings. The chief priority when examining the performance of coatings is long-term observation of suitable reference objects. It has been shown that SREP® due to its excellent durability can withstand decades and keep facades in a perfect condition. The latest development presented here is an additional approach for a further improvement of this paint system, to achieve additional cleanliness, if it is required from the local conditions.

7 References:

[1] I. König-Lumer, *Silicone-Resin Emulsions in Aqueous Facade-Coating Systems*, expert-Verlag (1997).

[2] H. Mayer, *The Chemistry and Properties of Silicone Resins*, Expert-Verlag, (1997).

[3] A. Lork, I. König-Lumer, H. Mayer, *Fine network shows strength of character*, European Coatings Journal 12/02, p. 14-21 (2002).

[4] J. Greene, D. Haeussler, B. Berglund, *Silicone Resin Emulsion Paint – Applications and References*, Paint & Coatings Industry magazine, Sept. 2002.

[5] A. Hausberger, *Silanes, siloxanes, silicone resins – Tailor-made for self-priming decorative coatings,* Formulation des composés siliconé et fluorés, p. 83-98, EDP Sciences 2004.

[6] A. Hausberger, *Profilo delle pitture a basa di resine silichoniche in emulsione*, Pitture e Vernici – European Coatings 2/2004, pp.13-22.

[7] www.srep.com, www.siliconharzfarben.de