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Silicone Resin Paint Systems: Adjustment of Optical Appearance as for the City Hall in Tallinn, Estonia, the Constance Minster and the Cologne Cathedral, Germany

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Abstract

Silicone paint systems are an option for creating hydrophobicity that is effective on the surface while decorating the substrate with colour. These systems have over 30-years development. The technical efficiency of the system has been proved in numerous tests. In Lower Saxony in particular, there is a long history of practical experience, especially on protected, historical substrates. Although the straight technological evaluation is generally rated as good, the "modern" silicone paint system, especially in the field of monument preservation, often lags behind the "classics" such as lime and silicate paints. Terms such as "painted to death" or "sterile" dominate the discussion of this highly emotional subject. Initiated by the problems presented at the Cologne Cathedral, a goal-oriented modification of the silicone paint system was accomplished.

1 Introduction

Coloured coatings applied to natural stone have been used for ages to decorate as well as to preserve this material. The discussion of whether the surface of natural stone needs protection from the influences of weathering in general, or whether coloured coatings can achieve this, are probably just as old as the painting tradition.

The development of "the" coloured coating shows a changing course throughout the centuries. While natural looking stone surfaces were primarily favoured in Graeco-Roman times, colourful architecture had its heyday in the Renaissance and baroque periods between the 16th and 18th centuries. At the end of the 18th century, the tendency was back to the natural looking stone surfaces of Graeco-Roman times.

Aside from attitudes towards the question of coloured coatings in general, paint systems also continued to develop over the centuries with respect to their binders. Without any pretension of being complete, lime and oil should be named for the period before the 19th century. At the beginning of that century, the introduction of water glass by Nepomuk Fuchs was an important step as far as material science was concerned since this material allowed the formulation of paints that were considerably more resistant to weathering. Another milestone was the development of plastics in the first half of the 20th century which allowed the formulation of dispersion or dispersion-silicate paints. The end of the development track are the silicone resin paints, dating from the sixties.

Although the weathering resistance of silicone resin paints is rated as "very high", their acceptance with regard to use on natural stone surfaces was limited. The most immediate argument against using a silicone resin paint system is that the resulting visual effect is not appropriate for historical objects. For this reason, when silicone resin paints are used on monuments, formulations were and are modified by a scumbling technique.

The main focus of the following paper is to explain the correlation between designing a formula and the physical properties of the silicone resin paint system. As a basis for this, the most important properties of the paint systems are discussed and supplemented with the practical experience gained at the City Hall in Tallinn, Estonia (Ordovician limestone) and the Constance Minster (molasse sandstone).

2 Material Properties of Selected Paint Systems

This subject, which could fill a textbook by itself, will only highlighted as needed to make the following text easier to understand. More information is found in BRANDES [1] and the publications listed in there.

Parameters	Binders				
	Lime	Oil	Dispersion paint	Silicate paint	Silicone resin paint
Structure	micro-porous	film-forming	film-forming	micro-porous	micro-porous
Surface appearance	mineral, matt range of colours	Glossy Yellowing	Glossy highly opaque	mineral, matt range of colours usually present	mineral, matt highly opaque to strong scumbling effect
Water permeability Liquid water	high	low	low	high to low (formulation)	low
Water vapour permeability	high	low	low	high	high
Long-term effect	Potential supplier of Ca and N in the case of lime-casein coatings; intensive scale formation or formation of exotic salt compounds are possible	Discoloration of the surface; formation of scale through moisture from behind	Scale formation or destruction of the surface caused by pent up moisture	Scale formation caused by over-strengthening of the surface through un-controlled deposit of the binder potassium water glass; spotting caused by activation of soluble iron minerals through alkalinity of water glass binder	Spotting is possible on extremely sensitive substrates because water is used as a solvent

Table 1: Property profile of different paint coating systems

When evaluating preserving measures for natural stone, it is necessary to interpret the change of essential parameters/characteristic values that characterise this material. This approach is also practical when comparing the property profiles of different paint systems. Table 1 contains these parameters for the area of coloured coatings – a special feature is presented by the evaluation item "long-term effect" which has been added to the list. Our own observations are presented here which make no claim to being complete or universally valid.

Other characteristics, especially technical ones, concerning application are found in [1].

As the title and introduction mention, the correlation between formulation and physical properties will be discussed in this paper. Why this subject? The answer lies in the need for creating natural stone surfaces that look as "alive" as possible when coating natural stone with a silicone resin paint system. This will be discussed in the following chapters.

Material	Task	Proportion
Water	Solvent	
Wetting agent	Auxiliary agent	
Preservative	Auxiliary agent	
Thickener	Auxiliary agent	
TiO_2	Filler/pigment	In total ≥ 60%
$CaCO_3$	Filler/pigment	
Talcum	Filler/pigment	
Silicone resin	Binder	Approx. 5% (solid constituent)
Dispersion (styrene, pure acrylate)	Binder	Approx. 5% (solid constituent)

Table 2: Guide formulation of a high quality silicone resin paint.

3 Formulation and Physics of a Silicone System

The basic components for formulating a high quality silicone resin paint are presented in Table 2.

In the guide formulation given above, the group of fillers/pigments and the two components that make up the binders are important for the discussion that follows. Let us proceed with the explanation using the binder component "pure acrylate". Seen isolated, this binder is a film-forming substance. If fillers are continuously added, this film remains closed for a long time in spite of local "perforation". This fact is what gives dispersion paint its typical properties. The part of the formulation that consists of the filler constituents, which is also expressed in the form of "pigment volume concentration" (PVC) is up to approx. 55% in this case. If a pigment volume concentration that depends on its exact formulation is exceeded, the closed binder film breaks down and a continuous pore structure occurs instead which results in a micro-porous structure of the coloured coating. This abrupt change in properties (water vapour tight to water vapour open) related to the degree it is filled with fillers is called "critical pigment volume concentration" (CPVC). Along with the abrupt change in water vapour diffusion properties, the loosening of the structure also causes a drastic reduction in the weathering resistance of the layer of paint. This is where the second binder component of a "true" silicone resin paint comes in. By exactly dosing the amount of silicone resin, the hollow pore spaces created by the corresponding quantity of fillers receive a water repelling lining without clo-

Modification		Changing parameters		
Addition of	Type of pigmentation	Penetration depth into the substrate	Water repellency	Possibilities for the substrate to dry
Water		Increase successively	Decrease successively	Increase
Aqueous impregnation		Increase successively	Remains constant	Diffusion unchanged Effective moisture passage decreases with increasing penetration depth
Binder components		Unchanged	Unchanged	Danger of densification of the system through a decrease of PVC
	Selection of opaque pigments and fillers with little hiding power	Unchanged	Unchanged	Unchanged

Table 3: Options for the Production of Paint Scumbles in a Silicone System

sing them off. The good physical properties of silicone resin paint (water repelling, water vapour diffusion open, weathering resistant) are therefore completed.

To complete the possibilities of influencing physical properties, it should also be said that the morphology of the substrate also plays a decisive role. While an evenly rough natural stone surface (e.g. sandstone) is more likely to promote water vapour diffusion because of the "binder perforating" properties of the individual components, extremely "porous" surfaces (e.g. shelly limestone) can lead to densification of the surface because of the disproportional, local increase in layer thickness that occurs.

In summary it can be said that the physical properties of a natural stone surface that is coated with a silicone resin system presents a very efficient but complex system that cannot be arbitrarily interfered with without the danger of changing its properties.

4 Options for the Production of Paint Scumbles in a Silicone System

In principle there are three options for producing paint scumbles in a silicone resin paint system (Table 3). These three options differ in their general approach for reducing the hiding power of the paint system and their effects on the physics of the system. The following text describes these three conceptual approaches in table form.

For a better understanding of this table, the following explanations are given:

- The starting point of the variation possibilities shown is a highly opaque, high quality silicone resin paint (e.g. Funcosil LA).
- The discussion on penetration depth concerns only the paint in the actual sense, without the use of a primer with a hydrophobic effect.
- The discussion on the drying rate takes into consideration the fact that the transport processes that lead to drying are always made up of moisture movements not only in the gas phase (low transport capacity) but also in the liquid phase (high transport capacity).

Study of Table 3 clearly shows that one variation possibility, that of a fundamental change of pigmentation, stands out because there are no accompanying negative changes of the material. The route to developing such a material system is described in the case studies that concludes this paper.

5 Case Studies

The primary objective of goal-oriented preservation of natural stone should always be to restrict the effective mechanisms that cause damage. The classic measure for achieving this has been and still is to apply a clear treatment based on an organosilicon base with a hydrophobic effect. This method has proved not to be the best for some stone substrates. An example of such a "failure" is reported by WENDLER et al. [2] where, among other things, the decrease in hydrophobicity of a calcareous substrate treated with a clear water repellent resulted in an increase of micro-biological growth. Similar problems are also reported by WILLIMZIG [3] for certain sections of the Cologne Cathedral. The section described by WILLIMZIG is actually the highly exposed abutment system made of Krensheim shelly limestone.

What is noteworthy is the fact that this section of the building to be preserved is a copy of the original in a replacement stone introduced in the 1930's. The composition of the stone (carbonate stone with high reactivity calcite surfaces), size and type of pore spaces (approx. 14% total porosity with a high constituent of coarse pores > 15 µm) and its exposed location on the building led to such a weathering rate that convinced the cathedral stonemason's lodge to seriously consider protective measures for the Krensheim shelly limestone, not only for pure preservation reasons but also for pragmatic, financial reasons (see Kölner Dombaublatt 1994 [WOLFF [4],]).

The first preservation experiments took place in 1978 using a clear, organosilicon, hydrophobic agent. The insufficient durability of such a measure on the shelly limestone specific to the object to be preserved is described above. In late summer of 1994, experiments were carried out with specially formulated lime paints. After one winter standing time, it became obvious that the erosion rate of this coating material, which had been consciously designed as a sacrificial layer, was clearly too high for the task at hand (protecting the surface of the shelly limestone for approximately the next 15 years). This observation coincides with the opinion of the AG Naturwerksteine / BMBF Project in whose minutes of the 11th meeting in 10/95 the following remarks were recorded by Professor Snethlage, head of the study group:

"Without hydrophobic treatment, pure lime or hydraulic lime grout on exposed building elements do not provide sufficient protection against moisture and are not durable enough by themselves."

Further on in the same minutes, an alternative to a clear hydrophobic treatment or lime paint/lime grout was given:

"Instead, preference is to be given to surface coatings which, depending on requirements, can be either a grout (up to approx. 5 mm), a highly filled paint (silicone resin dispersion paint) or a paint scumble. But all of these coatings must be hydrophobically formulated or they must be treated hydrophobically afterward. At the same time, the water repelling effect must include the surface areas of the limestone so that there is a smooth transition."

Following this philosophy, after viewing several objects that had been coated in the Funcosil Silicone System, and at the instigation of Professor Wolff, two pinnacles were prepared by a Remmers project team (cleaning, priming with a strengthening silicic acid ester, modification of the paint system) and coated. After one year, the pinnacles did not show any macroscopically recognizable ageing and the abutments were completed by the restoration team of Maul & Keller / Cologne (consolidation of the substrate in the Funcosil SAE Module System) and personnel from the cathedral stonemason's lodge in Cologne (application of the grout scumble).

To fulfil the requirement profile cited in the minutes above for the given substrate, a silicone grout was used as the coating material. The following properties were combined in this material:

- Water repellency based on the silicone resin binder
- Water repellency zone mainly on the surface with a smooth transition to the inside of the stone
- Water vapour diffusion unchanged
- Pore space filling – important to achieve a closed surface on the strongly weathered Krensheim shelly limestone
- Lime paint character through selection of pigments with corresponding optical effect
- Thin layer thickness (approx. 1-2 mm) avoids optical hiding / covering of the treasured historical form (e.g. drove cuts)

- Long service life (for the special case of the Cologne Cathedral, this has as yet to be proved, however, the experience provided by many other objects that have been coated in the Funcosil Silicone System (e.g. the moated castle in Dornum / East Friesia) make long-term durability of the described product systems quite probable.

In spite of having redesigned the product formulation specifically to the aim and object (product name: Funcosil ® Grout Scumble), the final optical result of the finished abutment is highly controversial. The reason for this is primarily coupled to two facts:

1. Working with one shade of colour on the abutment which was originally constructed from varying natural stone led to an obvious uniformity of the overall picture that has a somewhat unnatural look.
2. The shade of colour selected was based on the colour of the limestone surface. This naturally very light colour stands out clearly from the overall appearance of the cathedral.

However, it should be clearly expressed here that there are neither complaints concerning the work done by those responsible for the object nor complaints about the material system as such. In the recent past, the experience that was gained on this large, continuous natural stone surface has consequently been used constructively to clearly further improve adjustment of this system to the optical appearance of the substrate.

As an example of this, the work on the spire of the Constance Minster can be given where, as a further development of the previous concept for the "Cologne Cathedral Abutment", the following changes were made in the working procedure:

- Work using various shades of colour within the colour range of the natural stone substrate
- Incorporation of fillers identical to the substrate when designing the formulation.

Similar working approaches have produced results more appropriate for monument preservation on the Münster Cathedral and St. Mary's Church in Heiligenstadt.

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