THOMAS LAUBENDER[1)*)], JAMES GREENE[2)]

Adding value to coatings by using unique organofunctional silicone hybrids

Summary — The modification or replacement of polyurethane binders with unique amino and epoxy functional silicone hybrid coatings improves significantly the UV light and chemical resistance of industrial, shipbuilding and architectural coatings. In particular the upgrading of standard epoxy-amine coatings with new silicone hybrids improves the performance to that of urethane technologies. The replacement of Si-O-C bond with Si-C-C bond in silicone hybrids increases the weather resistance and the coatings ability to withstand exposure to harsh chemicals such as sulfuric acid, phosphoric acid, hydrochloric acid and ammonium hydroxide. In addition, the unique structure of organofunctional silicone hybrids increases the coatings resistance to graffiti, dirt pick-up and biological growth.
Key words: hybrid silicones with organic functional groups, crosslinking, weathering resistance, chemical resistance.

POPRAWA WŁAŚCIWOŚCI POWŁOK PRZEZ UŻYCIE HYBRYDOWYCH SILIKONÓW Z ORGANICZNYMI GRUPAMI FUNKCYJNYMI

Streszczenie — Powłoki przygotowywano z różnych żywic, pigmentu i niewielkiej ilości dodatków upłynniających poprzez sieciowanie za pomocą polisiloksanów z grupami aminowymi lub żywic akrylowych. Badano odporność na starzenie w warunkach atmosferycznych i odporność chemiczną powłok otrzymanych z cykloalifatycznych żywic epoksydowych, żywic akrylowych z grupami glicydoksylowymi lub polisiloksanów z grupami epoksydowymi. Stwierdzono, że opisana modyfikacja, polegająca na wymianie wiązań Si-O-C na wiązanie Si-C-C, zwiększa odporność na starzenie (rys. 1—4) i agresywne związki chemiczne (np. kwasy i zasady) (tabela 1). Użycie różnych typów organicznych środków wiążących w połączeniu z żywicami silikonowymi zawierającymi organiczne grupy funkcyjne pozwala na otrzymanie powłok o wysokiej trwałości, które mogą być stosowane nawet w drastycznych warunkach.
Słowa kluczowe: hybrydowe silikony z organicznymi grupami funkcyjnymi, sieciowanie, odporność na starzenie w warunkach atmosferycznych, odporność chemiczna.

Coatings used to protect industrial equipment, manufacturing facilities, oil-drilling platforms and shipbuilding applications are exposed to high levels of ultraviolet light and corrosive environments. These environments often cause harm to coatings, which may require frequent repainting to protect the substrate adequately.

The types of coatings currently used to protect metal substrates in the protective coatings and maintenance in shipbuilding industry are based either on one or a combination of zinc-rich primers, epoxy primers/topcoats, silicone alkyds, acrylics and polyurethanes [1]. Coatings based on aromatic epoxy resins provide excellent results when resistance to chemical and corrosive environments is necessary, however these coatings often fail when exposed to ultraviolet light, present in sunlight. The tendency of these types of coatings to chalking limits their usage as topcoats in exterior applications. Topcoats based on polyurethanes are normally used in combination with epoxy coatings when the application requires corrosion resistance and weather resistance with an ambient cure response. The isocyanates in the urethane systems are considered to be toxic due to the possibility of minute amounts of free isocyanate present, and they show generally high level of volatile organic compounds (VOC) [2, 3]. The acrylic technologies are generally good for exterior exposure; unfortunately due to their relatively high molecular weight they generally require a high level of solvent too for application.

Several years ago the initial introduction of hybrid coatings into the protective coatings market was based on silicone and epoxy polymers with amino hardeners or combinations of them [4]. These compositions may require a high degree of alkoxy functionality in the silanes and polysiloxane components, which, after curing, will have a high volatile organic compounds content due to the evolution of alcohol as a by-product. In addition, if the coating does not have a good through cure then the film will have a tendency to wrinkle. This is due to the continuation of the cure after being exposed to moisture

1) Wacker Chemie GmbH, Hans Seidel Platz, Munich, 81737, Germany.
2) Wacker Chemical Corporation, USA.
*) Author, to whom all correspondence should be addressed; e-mail: thomas.laubender@wacker.com

and sunlight or heat. In the meantime, new and innovative products have been designed for the protective coating market which improved the performance of the current technologies.

For example, amino functional polysiloxanes have been developed which can be used for epoxy resin or glycidoxy methacrylate (GMA) hardening to form extremely weather and chemical resistant epoxy amine polysiloxane hybrids. Furthermore, new upgraded glycidoxy functional polysiloxanes are found in the industry which can be cured for example with amines or with acrylics [5]. These innovations provide improved corrosion resistance, UV light resistance, low VOC levels and absence of isocyanates.

CLASSICAL SILICONES

The term "Silicones" generally is used for all kinds of synthetic polysiloxane polymers containing an inorganic silicon-oxygen-backbone and organic groups directly bounded to the silicon atoms *via* a silicon-carbon-bond. The inorganic silicon oxygen structure is the base for outstanding characteristics of silicones such as excellent temperature resistance, the unique stability against aging by weathering, sunlight and moisture and the very good chemical resistance.

Silicone resins are composed of highly crosslinked polysiloxane units and can contain some linear difunctional units for flexibility. The increased concentration of trifunctional units raises the number of high energy silicon-oxygen bonds, and therefore increases the polymer's resistance to UV and thermal degradation. The amount of energy needed to break the strong Si-O bond is approximately 108—110 kcal/mole, in comparison with C-C bond which is approximately 82—85 kcal/mole and C-O bond which is also just 84—87 kcal/mole.

Silicones can be seen as some kind of hermaphrodites. Beside their inorganic siloxane structure, additionally organic groups are directly bonded to the silicon atoms. These organic substituents strongly influence the silicone characteristics like compatibility, hardness, hydrophobic effect and chemical reactivity.

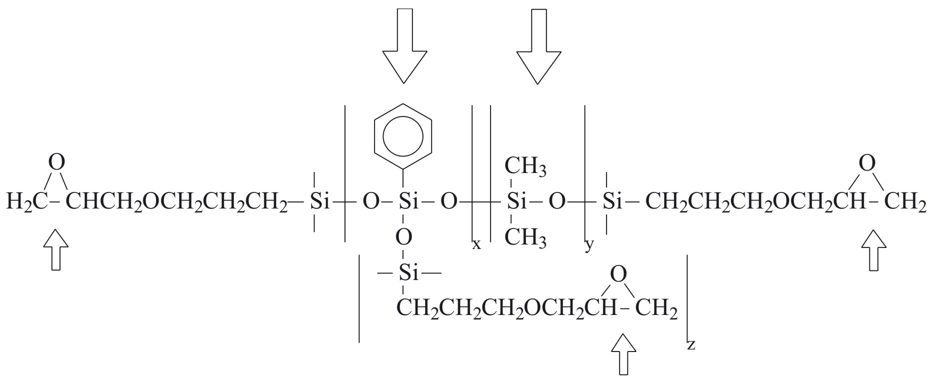
ORGANOSILICONE HYBRIDS

Organosilicone hybrids must contain an organic group which is capable to react with other organic binders *via* an addition curing mechanism and can cure under ambient conditions with no or little VOC [6, 7].

Silicone polymers cure to form coatings or silicone modified organic resins by one or a combination of the following reactions: hydrolysis and homo-polymerization, hydrolysis and copolymerization, and/or addition curing reaction.

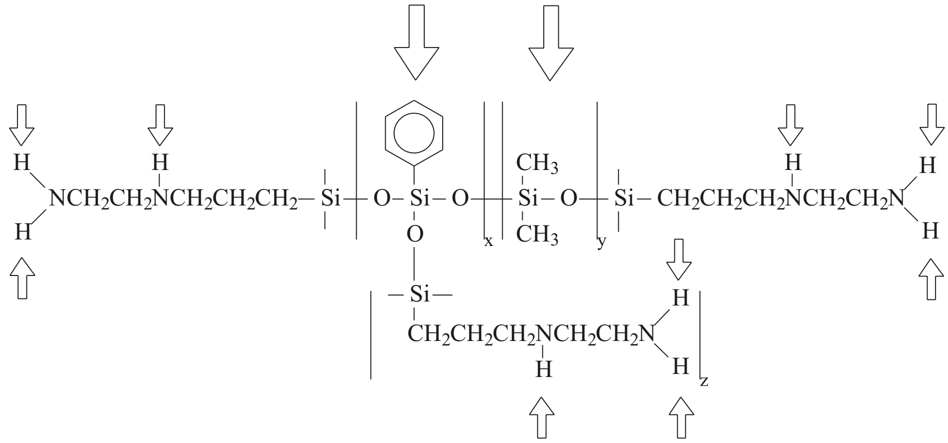
The incorporation of an addition curing group to the silicone polymer will eliminate the reversible reactions and allow the chemist to create an ambient curing system. There are few examples of the formation of an amino functional or an epoxyfunctional silicone resins, where the amino or the epoxy group is attached to the silicone through the hydrolytically stable Si-C-C linkage, and will react with suitable reaction partners like epoxy functional, amino functional or acrylic functional resins. Binder systems prepared using the epoxy or amino silicone/hardener for addition curing have increased chemical resistance, corrosion resistance and UV resistance when compared to the standard polyurethane and epoxy systems.

In consideration of all mentioned facts, two specifically designed organosilicone hybrids will be described now, which have successfully found their way into the protective coating and maritime maintenance coating industry. The first resin [Formula (I)] is a glycidoxy functional silicone polymer, which is used as a binder to increase UV resistance and corrosion resistance of coating formulations. This patented technology combines the chemical resistance and adhesion of an epoxy resin with UV and high temperature resistance of a silicone polymer in one product.



(I)

The second resin [Formula (II)] is an amino functional silicone polymer, which is used as a hardener, again to increase UV resistance, chemical resistance and corrosion resistance of coating formulations. When used with epoxy functional resins, it combines the chemical resistance and adhesion of an epoxy resin with UV light resistance of a silicone polymer in one product.



(II)

Such organosilicone hybrids used in coatings provide many advantages. They are less toxic than standard polyurethanes due to the absence of isocyanates for hardening and make possible the production of low-VOC-coatings with solids contents of about 90 % or even more. Epoxy amine binder systems can be upgraded so dramatically in weather resistance in terms of gloss and color stability that a top coat does not become necessary anymore. This possible elimination of one coat can save a lot of cost even if such siliconized coating binders are more expensive than standard binders.

EXPERIMENTAL

Method of testing. The progress of curing reaction was tested using an IR spectrometer. Intensity of NH and/or OH valence bands were registered and analyzed dependently on reaction time. It make possible to determine a rate of reaction.

To study a cracking tendency a resin coating (cured for at least one week) have been poured into an aluminum crucible about 1 mm thickness. After long time (from one week to several months) samples were observed to find possible cracking or shrinkage.

The morphology of coating was observed using transmission electron microscopy (TEM) and raster electron microscopy (REM). Weathering behavior of coatings was investigated by exposition to QUV-B and QUV-A artificial weathering equipment and by natural exposure in Germany, Singapore and Florida.

RESULTS AND DISCUSSION

Epoxy amine silicone hybrid coating based on cycloaliphatic epoxy resin and amino functional polysiloxane

Curing behavior

Coatings prepared by using a cycloaliphatic epoxy resin binder ("Eponex 1510", 33.1 wt. %), titanium dioxide pigment ("Kronos 2059", 29.9 wt. %), some flow additive (0.3 wt. %) and cured with an amino functional polysiloxane hardener ("SILRES (R) HP 2000", 36.7 wt. %), have been investigated in terms of their curing behavior. After mixing all components together, the coating has been applied in a thin film on a diamond as a substrate.

After the first fast curing reaction in the liquid phase the reaction rate became more and more slow when moving forward to the dry-to-touch time. It was very interesting to see that later on the reaction rate increase again for another couple of hours, so it can be assumed that the complete curing finally needs some days to become completed.

Non-cracking tendency

The cracking tendency was investigated both clear coatings and white pigmented epoxy amine hybrid coatings. Due to the optimum product design, we could not watch any cracking or shrinkage, neither after one week nor after several months. Supplementary we used the transmission electron microscopy for the inspection of the coating appearance in a very high magnification of 125 000:1 and found an extremely homogeneous film with first visible structures below 10 nanometers, which is equivalent to 100 (!) hydrogen atoms.

Weathering data

Epoxy amine silicone hybrid coatings prepared by using a cycloaliphatic epoxy resin binder, titanium dioxide pigment, flow additive and cured with an amino functional polysiloxane hardener have been investigated in terms of their weathering behavior. Using QUV-B artificial weathering equipment we could see outstanding gloss stability with just 40 % gloss reduction after 2000 h of artificial weathering. This result was clearly better than that of polyurethanes we had investigated for comparison (see Fig. 1).

After 1000 h of QUV-B weathering, the coating has been inspected using raster electron microscopy with a magnification of 1000:1. Fortunately, no cracks could be detected, just some laminar erosion of the surface had happened.

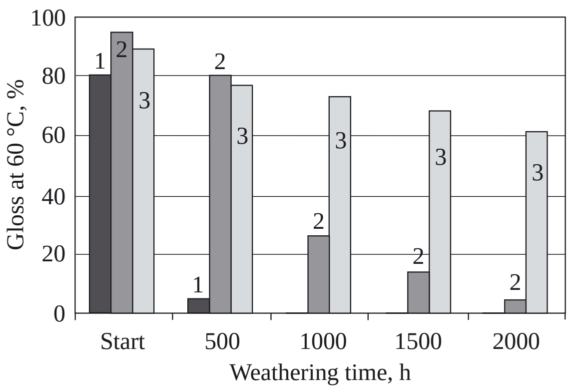


Fig. 1. Artificial QUV-B weathering of epoxyamine silicone hybrid coating (3) in comparison with control samples: epoxy amine (1) and polyurethane (2)

Beside the artificial weathering tests, the coating has been exposed also to natural weathering conditions. At Burghausen, Germany, which stands for warm dry to humid summers with temperatures of about 20 to 35 ^{o}C and cold winters with temperatures down to -25 ^{o}C, we could not watch any significant gloss reduction or cracking even after 3 years of exposure. At Singapore, which stands for a high UV radiation, hot and humid conditions all over the year, we observed so far a gloss reduction from 90 % to 78 % after 1.5 years of exposure and again no cracks or other problems.

Epoxy acrylic amine silicone hybrid coatings based on glycidoxy functional acrylic resin and amino functional polysiloxane — weathering data

Epoxy acrylic amine silicone hybrid coatings prepared by using glycidoxy functional acrylic resin binder ("Almatex PD-1700" as 60 wt. % solution in xylene, 52.8 wt. %), titanium dioxide pigment ("Kronos 2059", 28.4 wt. %), some flow additive (0.3 wt. %), xylene (5.3 wt. %) and cured with amino functional polysiloxane hardener ("SILRES (R) HP 2000", 13.2 wt. %) have been investigated in terms of their weathering behavior.

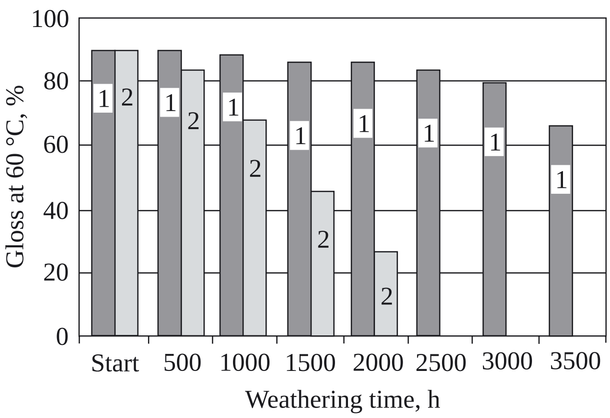


Fig. 2. Artificial QUV-A (1) and QUV-B (2) weathering of epoxy acrylic amine silicone hybrid coating based on glycidoxy functional acrylic resin and amino functional polysiloxane

Testing the QUV-A artificial weathering, we found an outstanding gloss stability up to 3000 h with a reduction just from 90 % to about 80 % (see Fig. 2). Also the QUV-B weathering data seem to confirm this excellent gloss protection behavior, even when the gloss is reduced quite early.

Epoxy amine silicone hybrid coating based on epoxy functional polysiloxane and acrylic resin — weathering data

Coatings prepared by using epoxy fractional polysiloxane binder ("Silres HP 1000", 10.2 wt. %), titanium dioxide pigment ("Du Pont R-960", 24.8 wt. %), some foam control agent (0.1 wt. %) and cured with various acrylic resins *e.g.* acidic functional acrylic resin ("Paraloid AE 1285", 57.9 wt. %) have been investigated in terms of their artificial and natural weathering behaviors.

The exposure of these systems to QUV-A and South Florida indicated that the best performing product was

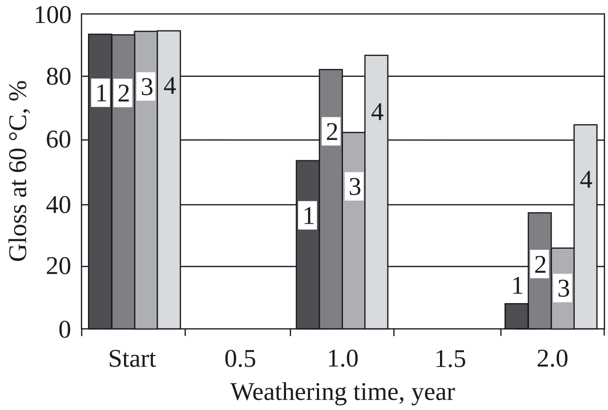


Fig. 3. Gloss at natural weathering (Florida 45^{o} South) of epoxy acrylic silicone hybrid coatings based on epoxy functional polysiloxane and acidic functional acrylic resin (3 — not washed, 4 — washed) in comparison with polyurethane (1 — not washed, 2 — washed)

the epoxy functional silicone resin with acidic functional acrylic (see Fig. 3). The polyurethane looked good for a period of time however failed earlier than the epoxy functional silicone resin/acidic functional acrylic. The Florida exposure panels after one and two years exposure at 45^{o} South demonstrated that the epoxy functional silicone resin/acid functional acrylic showed less dirt pick up and better gloss retention than the polyurethane, both for washed and for panels not cleaned before measurement.

The colour difference or delta E measurements were taken on the washed and unwashed portion of the panels. Polyurethane showed a significant increase in delta

T a b l e 1. Chemical resistance and solvent resistance of various types of coating systems

Chemicals/ solvents	Concentration of active substance wt. %	Polyurethane	Epoxyamine	Aliphatic epoxy + aminosilicone	Epoxyacrylic + aminosilicone	Epoxysilicone + acidic acrylic
Hydrochloric acid	37	slight defect	strong defect	no change	slight defect	slight defect
Sulfuric acid	98	strong defect	strong defect	strong defect	strong defect	slight defect
Phosphoric acid	84	slight defect	strong defect	no change	strong defect	slight defect
Sodium hydroxide	50	slight defect	no change	no change	no change	no change
Ammonium hydroxide	25	no change	no change	no change	no change	no change
Xylene	100	>100 DR	>100 DR	>100 DR	50 DR	>100 DR

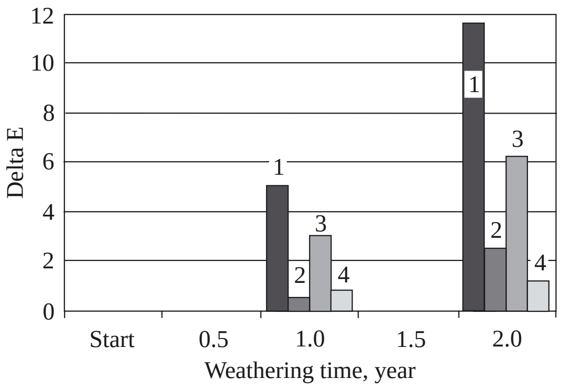


Fig. 4. Colour change (delta E) at natural weathering (Florida 45^{o} South) of epoxy acrylic silicone hybrid coatings based on epoxy functional polysiloxane and acidic functional acrylic resin (3 — not washed, 4 — washed) in comparison with polyurethane (1 — not washed, 2 — washed)

E due to dirt retention and oxidation (see Fig. 4). The delta E improves (decreases) for the epoxy silicone/acrylic coating due to the ease of cleaning and less dirt retention and less oxidation.

Comparison chemical and solvent resistance

Coatings prepared from the various hybrid compositions were also evaluated for resistance to chemicals like concentrated hydrochloric acid, phosphoric acid, sulfuric acid and sodium hydroxide (Table 1). The control samples mere commercial epoxy and aliphatic urethane systems and epoxy/acidic acrylic systems. Both systems were susceptible to acids and more resistant to alkaline environments.

In case of organofunctional silicone hybrids, the resistance of the coatings to acidic environments as well as alkaline environments has been increased. In view to solvent resistance all coating systems worked well with the exception of the epoxy acrylate (GMA), cured with the amino functional polysiloxane.

CONCLUSION

The modification or replacement of polyurethane binders with unique amino and epoxy functional silicone hybrid coatings improves significantly the ultraviolet light resistance and chemical resistance of industrial, shipbuilding and architectural coatings. The type of organic binder used in conjunction with the organofunctional silicone resin is important in designing a high performance system.

In addition to that, the unique structure of organofunctional silicone hybrids also increases the coatings resistance to graffiti, dirt pick up and biological growth.

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