

“Properties and use of inorganic polysiloxane hybrid coatings for the protective coatings industry”.

By: J.M. Keijman
Technical Director Ameron BV – Performance Coatings Group
J.F. Kennedylaan 6
4191 GT Geldermalsen
The Netherlands

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Abstract:

Silicon-based inorganic polysiloxane hybrid coatings have entered the Protective Coatings industry as alternatives to the traditionally used organic polymer-based coatings.

A review of the different inorganic and hybrid coatings, their characteristics and features, their combinations in coating systems and their use and benefits in the Protective Coatings industry will be discussed.

I. Introduction

Organic resin based coatings have been used for many years as high performance and corrosion resistant maintenance coatings.

From the protective coatings standpoint, each generic type of coating possesses certain unique features and benefits as well as certain limitations. These are highlighted in the following table.

Generic coating	Features	Limitations
epoxy	<ul style="list-style-type: none">● corrosion barrier● durability● adhesion	<ul style="list-style-type: none">● chalking (weatherability)● critical low temperature curing
Polyurethane	<ul style="list-style-type: none">● appearance● durability● weatherability	<ul style="list-style-type: none">● moisture sensitive● health hazard (isocyanate)
Moisture curing polyurethanes	<ul style="list-style-type: none">● one component● low temperature application	<ul style="list-style-type: none">● moisture sensitive● health hazards● stability/shelf life
Epoxy acrylic	<ul style="list-style-type: none">● appearance● weatherability	<ul style="list-style-type: none">● long term gloss retention● compatibility with intermediates

Table 1: Features and limitations of organic coatings

These features and limitations result from the fact that the binder systems are organic in nature.

Through binder and formulation re-design, exploring the inorganic binder types with emphasis on the silicon based chemistry, organic-inorganic polysiloxane hybrid coatings have been developed during the last decades of the last century.

This has resulted in the introduction of epoxy polysiloxane hybrid binders in the coatings industry, which has caused a breakthrough in the protective coatings industry.

By the combination of epoxy based organic and silicon based inorganic binder systems, high technology coatings have been introduced providing the durability and toughness of epoxy coatings whilst outranking the gloss and colour retention of the best urethane based topcoats.

II. Organic – inorganic hybrids

Hybrid materials are composites formed or composed of heterogeneous elements. Organic – inorganic hybrids combine the distinctive properties of inorganic, ceramic materials with the typical characteristics of organic materials.

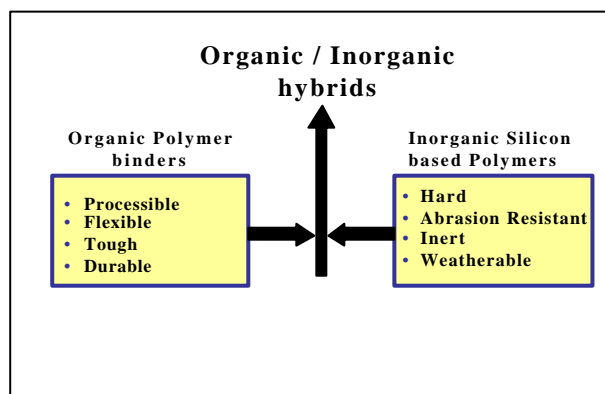


Figure 1 – Organic/inorganic hybrids

The organic – inorganic hybrids concept has also been employed to combine the organic and inorganic properties of materials to more sophisticated coating with a higher added value in the Protective Coatings industry.

This class of organic-inorganic hybrid coatings covers the entire area between the pure organic and the pure inorganic coatings.

Organic-inorganic hybrids can be distinguished in different morphological combinations, which include the following categories:

- category 1, **the inorganic matrix**, where organic materials are embedded in an inorganic polymer. An example of this category is obtained by the incorporation of small quantities of organic products into the inorganic matrix of zinc silicate coatings.

- category 2, **the organic matrix**, where inorganic materials are embedded in an organic polymer. Some of the oldest and well-known organic – inorganic hybrids of this category are used in the paint industry by the dispersion of inorganic pigments into organic binders;
- category 3, **the interpenetrating network**, where inorganic and organic polymeric networks are independently formed without mutual chemical bonds. The incorporation of inorganic macro-molecular sol-gel networks into organic polymer structures is an example of this category;
- category 4, **true hybrids**, where inorganic and organic polymeric systems with mutual chemical bonds are formed. Specifically these true hybrids have been explored successfully for the development of new binders for use in high technology organic-inorganic polysiloxane hybrid based coatings.

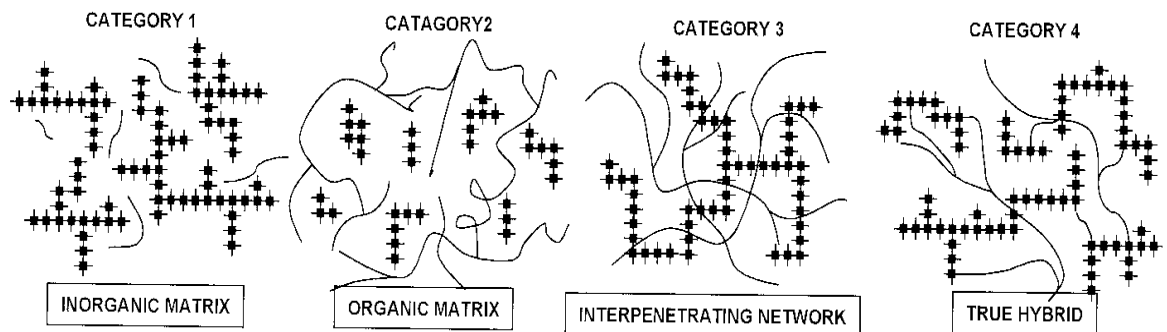


Figure 2 Organic/inorganic hybrid structures (reference 1)

III. Inorganic coatings

Inorganic coatings are predominantly formulated with silicon based binders, such as water- and solvent-based silicates, silicone resins, silanes and mixtures of organic binders with silicate and silicone binders.

Commonly, all these traditional inorganic coatings have limited use to very specific applications due to the characteristics of the binder systems.

- silicone high temperature resistant resin based coatings, requiring heat curing at levels of 230°C;
- silicate based coatings, which are formulated with high pigment contents, resulting flat and rather porous coatings;
- silane based low viscous sealers.

The use of these inorganic coatings have been limited to specific applications, such as:

- stacks and other structures exposed to high operating temperatures;
- tanks exposed to combinations of high temperatures and aggressive chemicals;
- structures in the nuclear industry, exposed to high levels of radiation;

- mineral walls of buildings as decorative paint and atmospheric protection;
- concrete and masonry structures to provide water repellence.

The zinc silicate primers, formulated with metallic zinc powder and silicate binders must be distinguished as a special class of inorganic coatings. Zinc silicates have been the state of the art in corrosion protection for more than half a century and have found wide acceptance in the Protective Coatings Industry.

By combining the inorganic polymeric structure of siloxanes with organic binder systems, coatings have been developed, which combine the inertness, weatherability and hardness of inorganics with the processability and toughness of organic binders.

IV. **Polysiloxane hybrid coatings**

The term polysiloxane reflects the nature of the polymeric structure that contains repeating silicon-oxygen groups as backbone.

Organic-inorganic hybrids have been developed by chemical modification of the polysiloxane backbone with functional organic groups. By the versatility of the polysiloxane chemistry, a variety of functional organic groups can be attached to the inorganic siloxane backbone.

This chemistry allowed the development of hybrid binder systems with varying reactivity and chemical and physical properties. The mutual chemical bond between the organic functional groups and the inorganic polysiloxane matrix represents the category of true hybrids.

The advances in the siloxane chemistry by bonding functional organic groups to the silicon atom in polysiloxanes have resulted in a significant breakthrough in the protective coatings industry. By utilising the organic-inorganic polysiloxane technology, a variety of polysiloxane coatings have been developed for use in the coatings industry. The most important coatings for the protective coatings industry are:

- the two component epoxy-polysiloxane hybrid coating
- the one component acrylic polysiloxane hybrid coating

Most experience has been obtained with the epoxy siloxane hybrid coating, which has been used successfully in the protective coatings industry since its introduction in 1994.

V. **Epoxy polysiloxane hybrid coatings**

The development of epoxy siloxane hybrid coatings based on a polysiloxane backbone constitutes a technological advancement, comparable to the introduction of inorganic zinc silicates in the middle of the last century.

The chemical combination of aliphatic epoxies with polysiloxanes resulted in polymers with higher performance characteristics than can be achieved by the physical combination of both polymers.

The chemical combination provided the basis for the joined polymeric strength, weathering durability, radiation resistance, gloss and colour retention and corrosion protective properties of the polymers, whilst overcoming the brittleness of inorganic structures.

The typical properties of the epoxy siloxane hybrid coatings are shown in table 2.

Volume solids	90%
VOC (EPA method 24)	120 gram/litre
Components	2
Mixing ratio by volume	4 : 1
Application methods	airless and conventional spray, roller and brush
Thinning	not required
Dry film thickness per coat	75-200 microns
Theoretical coverage (125 µm)	7,2 m ² /litre
Potlife (20°C)	4 hours
Drying times (20°C) - to touch - through	2 hours 4.5 hours
Recoat/topcoat time (20°C) - minimum - maximum	3 hours none
Gloss	90%
Flash points	Resin 97°C, cure 96°C

Table 2 Typical properties epoxy siloxane hybrid coating

The epoxy siloxane hybrid coating has excellent compatibility with most zinc epoxy and zinc silicate primers, surface tolerant and anti-corrosive epoxy primers and with itself.

VI. Improvements achieved with the epoxy polysiloxane hybrid coatings

The advances achieved with the introduction of the epoxy polysiloxane hybrid coatings include:

- high volume solids, low VOC inorganic hybrid coating
- high build application characteristics by standard application equipment

- reduced effects on health, safety and environment
- significant improved weathering compared to polyurethanes
- outstanding corrosion resistance
- excellent resistance to nuclear radiation
- excellent defence against graffiti
- excellent surface spread of flame resistance

High volume solids

Utilising low viscosity of the binder system, a high solids, high build epoxy polysiloxane hybrid coating has been formulated with a volume solids of 90% and a VOC of 120 gr./lt., meeting all known environmental requirements.

Application

The epoxy polysiloxane is a two component coating with long potlife, which is applied at dry film thicknesses of 75 to 200 microns without sagging.

The epoxy polysiloxane hybrid coating is easy to apply and does not require specialised equipment. It can be applied by airless and conventional spray, brush or roller. As no thinning is required for application, emissions of volatile organic compounds are controlled and no extra costs for thinners have to be made.

The epoxy polysiloxane hybrid coating is compatible with a wide range of primers and intermediate coats, which include zinc epoxies, zinc silicates and anti-corrosive coatings.

It is a fast drying coating at ambient temperatures throughout Europe, Middle East and Africa.

Health, Safety and Environment

By its high volume solids content of 90 percent in combination with its ease of application without the use of thinners, a significant reduction of solvent emissions and waste is achieved. By its low VOC, the polysiloxane coating is fully complying with the increasingly stringent environmental health and safety requirements without downgrading coating performance.

The epoxy polysiloxane hybrid coatings represent a large improvement with respect to health, safety and environment compared to epoxy, epoxy acrylic and polyurethane coatings.

Experience from a major coating contractor in the European offshore industry is that personnel with epoxy allergy can work with the epoxy polysiloxane hybrid coatings without provoking any skin reactions. This included personnel with a very strong reaction to liquid epoxy resin based coatings.

The epoxy polysiloxane hybrid coating does not contain known health hazardous materials like isocyanates, which can cause respiratory sensitisation.

The epoxy polysiloxane coatings are formulated with lead- and chromate-free pigments. The high flash points of both components reduce the fire hazards and contribute to safe transport and storage of the epoxy polysiloxane coating.

Weathering

The polymeric structure that contains repeating silicon-oxygen groups in the backbone of the epoxy polysiloxane hybrid coating provides the basis for the excellent weathering characteristics.

As a consequence, the coating is hardly affected by sunlight, weathering or atmospheric oxidation in contrast to organic-based coatings, that eventually degrade under these exposure conditions.

Epoxy polysiloxane hybrid coatings retain their colour and gloss far better than other topcoats in the protective coatings industry, such as polyurethanes, which show fading and loss of gloss in 3 to 5 years.

This is also demonstrated from the comparison of the epoxy polysiloxane hybrid coating with a wide range of polyurethane topcoats by Florida exposure tests carried out by ACQPA, France. After 12 months exposure, the epoxy polysiloxane hybrid coating outperformed the polyurethanes in colour and gloss retention as is shown in figure 3.

Percentage of gloss retention of Polyurethane and Polysiloxane (1year Florida)

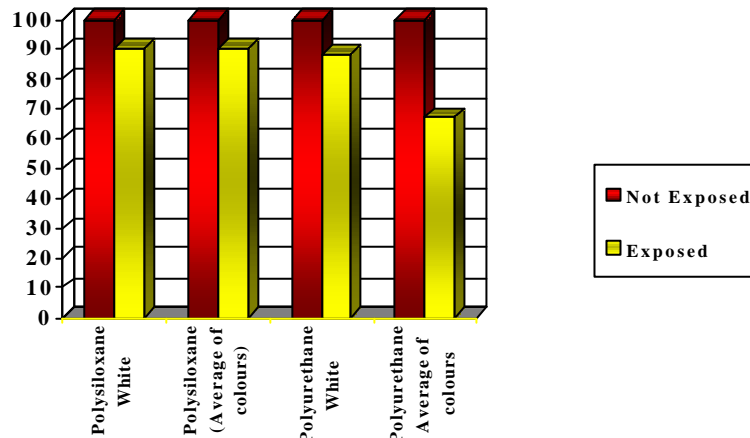


Figure 3: Percentage of gloss retention of polyurethane and polysiloxane

The percentage of gloss retention can be calculated by dividing the gloss level of a coating after exposure to weathering by the initial gloss level of the non-exposed coating multiplied with a factor of 100.

The epoxy polysiloxane hybrid coating retained 90% of its initial gloss for white and an average of 90% for a variety of colours after 12 months 45° South Florida testing with no chalking or checking.

The polyurethanes showed a percentage of gloss retention of 88% for white colours and an average of 67% for the colour-pigmented formulations.

Outstanding corrosion resistance

A considerable improvement in durability has been achieved with the introduction of epoxy polysiloxane coatings. This is demonstrated by the excellent performance of two coat epoxy polysiloxane based coatings as tested by various independent laboratories and coating specifications.

- *Norsok spec. standard M-CR-501*

The specific test methods for this standard include 6000 hours saltspray testing, 6000 hours condensation chamber and 4200 hours cyclic testing by intermittent exposure to saltspray and UV-light. This test program in combination with the specified acceptance criteria is currently considered as the most severe performance test requirement for protective coating systems in the coating industry.

The two coat systems consisting of 75 microns of either a zinc silicate or a zinc epoxy primer followed by 125 microns of high solids epoxy polysiloxane hybrid coating, applied on SA 22 dry abrasive blast-cleaned steel, have been tested successfully and qualified following this Norsok pre-qualification test program.

The coating system consisting of 70 microns of a modified inorganic zinc primer and 130 microns epoxy polysiloxane, applied over UHP water jetting cleaned existing blastprimer has also been qualified following the Norsok pre-qualification test program.

- *ACQPA*

The combination of 40 µm zinc rich epoxy and 140 µm of the epoxy siloxane hybrid coating has been tested and approved following the ACQPA performance test requirements in France.

- *ISO 12944*

The coating system, consisting of a zinc rich epoxy primer at 75 µm and one coat of the high solids epoxy siloxane hybrid coating at 125 µm has been tested in accordance with the ISO 12944 standard "corrosion protection of steel structures by protective paint systems" and passed the test requirements for high marine corrosivity (C5M) durability class high.

- *US Navy testing*

In a test program of the USA Navy 18 coating systems have been evaluated for corrosion control of topside naval systems. The tests included salt fog testing, electrochemical impedance spectroscopy (EIS) and shipboard exposure tests. For each test, the coatings examined were ranked by performance. It was concluded that the two coat system consisting of a zinc-based primer with the epoxy siloxane topcoat outperformed the other coating systems in all tests carried out.

Nuclear radiation

The epoxy polysiloxane hybrid coating is essentially unaffected by nuclear radiation and has an excellent rating for decontamination. The coating performed without any defects on irradiation to a cumulative dose of 5.000 megarad as tested by the Dutch ECN-laboratories. On nuclear decontamination testing according to BS 4247, a decontamination factor of 5849 was rated. Organic coating systems are showing considerable lower decontamination factors with typical values of 500 to 1.000.

Defence against graffiti

By the combination of organic and inorganic polymer structures, the epoxy polysiloxane hybrid coating offers an excellent defence against graffiti.

On testing by the London Underground Ltd., it was concluded that the epoxy polysiloxane hybrid coating was rated as the best liquid applied coating.

The use of the epoxy polysiloxane coating on various projects in practice, such as on railway coaches showed that the coating easily could be cleaned from graffiti without leaving a shadow after cleaning.

Surface spread of flame

The results obtained by various laboratories as shown in table 3 indicate that the epoxy polysiloxane hybrid based coating system has excellent surface spread of flame and fire propagation resistance, meeting the requirements in various countries.

<u>Test Results Surface Spread of Flame</u>	
<u>Epoxy Polysiloxane Coating</u>	
Warrington Fire Research Institute - UK	
• BS 476, part 6 and 7	0 class fire rating
South West Research Institute - USA	
• Flame Spread E84	NFPA class A criteria
• Flame Spread index	10
• Smoke development index	15
Laboratoire National d' Essais - France	
• Standard NF F16-101/102	Rating F0, M1

Table 3: Test results surface spread of flame

VII. **Cost efficiency**

The number of advances achieved with the introduction of epoxy polysiloxane hybrid coatings including

- the high volume solids (90%) and low VOC (120 gr/ltr.) inorganic coating
- the high build application characteristics by standard application equipment
- the significantly improved weathering compared to polyurethanes
- the excellent corrosion resistance

have permitted the replacement of the three of more coat traditional coating systems by a two coat zinc-based epoxy polysiloxane hybrid topcoat system.

With the introduction of epoxy polysiloxane hybrid coating, the CRINE-initiative is embraced. The CRINE-initiative, which stands for Cost Reduction In The New Era, was developed in U.K. as a drive to reduce development and life cycle cost of capital investments in the offshore industry. Factors contributing to cost savings, using the epoxy polysiloxane hybrid coatings, are:

- Application cost saving factors:
 - less number of coats
 - reduced man-hours
 - increased productivity – faster turning around times
 - minimising scaffolding
 - less disruption to other trades
 - reduced coatings weight
 - reduced waste disposal cost
- Performance factors:
 - improved colour and gloss retention
 - coating system life extended or maintained
- Health, Safety and Environmental aspects:
 - reduced risk of industrial accidents
 - reduction of waste
 - reduced VOC emissions
 - contains no isocyanates or lead chromates
- Inorganic polysiloxane nature
 - minimising repair requirements for damages by welding (reduced burnback damage).

A comparison of projected longevity figures of the two coat zinc rich epoxy primer with the epoxy siloxane topcoat and two current state of the art coating systems is made in table 4.

Product	Dft. μm	Sea Cost Marine life projections (practical time to repaint 5 to 10% coating break-down)	Offshore life projections (years) - practical time to repaint 5 to 10% coating break-down	CRINE new construction life projections
System 1 Blast to SA 2.5				
Zinc rich epoxy primer	75	6.0	4.2	
1st high build epoxy	125	11.3	7.9	
2nd high build epoxy	125	3.8	2.6	
Polyurethane/epoxy acrylic	<u>50</u>	<u>1.5</u>	<u>1.1</u>	
	375	22.5	15.8	15
System 2 Blast to SA 2.5				
Zinc rich epoxy primer	75	6.0	4.2	
Epoxy siloxane	<u>125</u>	<u>16.3</u>	<u>11.4</u>	
	200	22.3	15.6	15
System 3 Blast to SA 2.5				
Epoxy primer	50	3.5	2.5	
Glass flake	250	15.2	10.6	
Polyurethane/epoxy acrylic	<u>50</u>	<u>1.5</u>	<u>1.1</u>	
	350	20.2	14.1	12

Table 4: Offshore coating systems life projections new construction - practical time to repaint.

The above projections are based on the NACE published paper "A review and update of the paint and coatings cost and selection guide" April, 1993.

This is based on coating system life projections based on Sea Coast Marine Environment i.e. within a 5 mile radius of sea coast. As an offshore environment is not published, the Sea Coast Marine environment figure less 30% has been taken.

The system life projections have been adopted from the Shell Engineering Reference Document Standard ES/011 Rev: DRAFT/7 System 2A1 Table A3 basis for life cycle cost.

Based on known yard new construction applied cost values, the estimated applied cost of the coating systems in UK Pounds Sterling is reviewed.

By the introduction of the epoxy polysiloxane based system, a cost saving of £ 2.08/m² in comparison to a traditional 4 coat offshore coating system and of £ 0.74/m² in comparison to a glass flake high solids epoxy system can be achieved (table 5).

		Zinc epoxy primer Epoxy Epoxy Epoxy/Pu (in microns)	Epoxy polysiloxane over organic zinc rich epoxy or IOZ primer (in microns)	ZP primer Glass flake High Solids Epoxy Epoxy/Pu (in microns)
System	Primer Mid coats Topcoat	1 x 75 2 x 125 1 x 50	1 x 75 1 x 125	1 x 50 1 x 250 1 x 50
Labour cost	Hrs/m ² £/m ²	0.49 9.19	0.37 6.94	0.45 8.44
Material cost £/m ²	Equipment Grit Coating	2.57 4.00 4.05	1.94 4.00 4.85	2.36 4.00 3.67
Total system cost	£/m ²	19.81	17.73	18.47

Table 5: Estimated applied cost of offshore coating systems

VIII. Field experience and case histories

Since its introduction in the protective coatings industry, the epoxy polysiloxane hybrid coating has been used for the protection of more than 3 million m² of steel, which includes large offshore newbuilding and maintenance projects, the nuclear and mining industry, refineries, on shore plants, tunnels and bridges and a variety of OEM projects.

VIII. Conclusion

The success of the epoxy polysiloxane hybrid coating is a result of the unique characteristics achieved by chemical modification of the inorganic polysiloxane backbone with functional organic aliphatic epoxy groups.

This new technology provided the basis for a breakthrough in the protective coating industry, utilising the greatly improved coating performance characteristics based on the epoxy polysiloxane hybrids binder systems.

References

1. S. Frings, C.F. van Nostrum, R. van der Linde - The performance of polyester based organic-inorganic hybrid coatings for prefinish construction steel and aluminium. Paper 61, Proceedings 5th Nurnberg Congress "Creative advances in Coatings Technology, 1999".
2. J. McCarthy - New topcoat technology for maintenance of marine and offshore structures, SSPC Conference 1997.
3. N. Lindsey, R. Conrad, C. Bowles – Evaluation of coatings for corrosion control of topside naval systems – NACE, Corrosion conference 96, paper 619.
4. D. Hart, J. Griffiths – Armada Teamwork in Action – European Construction Industry Conference, Brussels, 1996.
5. L. Flynn – Two coat coating system keeps Peace Bridge in pink - Roads and bridges, November 1994.
6. Coating system on Peace Bridge weathered recent inspections well – JPCL, October 2000 – PCE.
7. J.J. Snedden – PSX 700 engineered siloxane – CD ROM, Ameron International BV, internal product information, May 2000.
8. J.M. Keijman - High Solids Coatings: Experience in Europe and USA - Paper 40, Proceedings PCE Conference in The Hague, The Netherlands "Protecting industrial and marine structures with coatings", March 1997.
9. G.H. Brevoort - A review and update of the paint and coatings cost and selection guide – NACE, Corrosion conference 1993.