High Solids Coatings:
Experience in Europe and USA

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INTRODUCTION

The success of protective coatings industry has in the past depended primarily upon their performance characteristics and ability to protect steel structures effectively. Little consideration was given to pollution of potential effects to workers' health and the environment.

Many factors have influenced coatings technology over the last two decades, but the single most influential force has been the control and regulation of the health and environmental impact.

Paints and coatings have come under increasing scrutiny since the mid-1970's, when the California Air Resources Board (CARB) first identified the solvents in coatings as a contributor to air pollution. Volatile organic compounds (VOC's) are commonly used solvents in coatings and paints that evaporate during application, drying and curing. They may react with nitrogen oxides in the presence of sunlight and heat to generate lower atmospheric ozone.

The South Coast Air Quality Management District, one of the 41 Air Quality Districts in California, USA, have established and enforced air pollution regulations to reduce the emission of volatile hydrocarbons from paints which probably have initiated the reduction of solvent emissions in the world. These regulations include:

- Limitations on the volatile organic compounds (VOC) content in paints and coatings.
- Quota for maximum quantities of solvents per year for stationary facilities, such as steel fabricator's shops.
- Restrictions on the maximum amount of VOC emissions produced per day.
- A minimum transfer efficiency for coatings on metallic parts and materials.

California's actions on the reductions of volatile organic compounds (VOC's) have served as the model for other areas in the United States and in Europe.

The growing concern throughout Europe on the health hazards associated with the various components in protective coatings has also lead to legislation and regulations in Western Europe. The legislation and rules can vary considerably between the different European countries, but all deal with the pollution control of air, the soil and ground water, the control of waste and limitations on the use of heavy metals (lead and chrome) in coatings and paints.

Several products and technologies have been developed to comply with these regulations and legislations which include waterborne coatings, high solids and solvent free coatings and the use of solvent recovery, recycling and incineration systems.

HIGH SOLIDS COATINGS

In the paint and coating industry no definition exists on the minimum or average solids content level for "high solids" coatings. The term "high solids" is often used for commercial purposes. The opinions on "high solids" also vary within the different markets of the paint industry and with the generic types of coatings and paints.

For the heavy duty protective coatings industry it is assumed that "high solids" coatings have a minimum volume solids content of 65%. A volume solids content of 80% is considered as the general accepted standard for high solids coatings.

As is shown in table 1, these figures are meeting the volume solids requirements as calculated from the current VOC requirements.

Country	Lbs/gallon	Grams/litre	Volume Solids (%)
United States	2.8	340	63
United Kingdom			
- Starting 1/4/96			
* general	--	400	56
* finish coats	--	520	42
- Starting 1/4/98			
* general	--	250	72
* finish coats	--	420	53

Table 1 - VOC (Volatile Organic Compounds)

The drive towards "high solids" coatings, initiated and fostered by environmental regulations has also caused a change in the types of coatings which are used in the protective coatings industry. The physical drying coatings, such as the vinyls and chlorinated rubbers have gradually been replaced by chemical drying two component coating systems.

The epoxy and polyurethane based coatings are currently representing the major part of the "high solids" coatings in the protective coatings market.

Coatings technology trends in North America are showing a dramatic swing away from single package low solids products towards two component high solids coatings. This is demonstrated in table 2, showing the use of resin types in coatings for offshore equipment. This survey is based on a 1989 survey with a ten year forecast.

	1989	1992	1994	1999
Acrylic	0.90	1.00	1.10	1.30
Alkyd	3.40	2.90	2.70	2.30
Epoxy	8.70	10.60	11.80	14.70
Polyester	0.20	0.20	0.20	0.20
Polyurethane/aliphatic	3.40	4.00	4.30	5.20
Polyurethane/aromatic	0.90	1.10	1.20	1.40
Vinyl polymer/copolymer	1.50	1.50	1.50	1.50
Chlorinated rubber	0.20	0.20	0.20	0.10
Other	2.60	2.30	2.20	2.00
Totals	21.80	23.80	25.20	28.70

Table 2 - Resin trends - North America (in thousands of metric tons)

Often lost in the arguments on solvent reductions, are the advantages and positive features obtained with “high solids” coatings.

Originally these high solids coating systems, specifically the high solids, high build epoxy coatings, have been developed as high performance self priming maintenance coatings, compatible with minimum surface preparation. The tolerance for steel surfaces compromised with tightly adhering rust or previously applied residual paints is obtained by a concept where low molecular weight low viscosity epoxy and synthetic resin blends are combined with selected curing agent mixtures.

Well formulated high solids high build epoxy coatings exhibit excellent corrosion protection and performance in addition to their compliance with the low VOC regulations. They are also compliant with health regulations by absence of lead or chromate based pigments. Typically the high solids epoxy coatings can be applied at high film builds providing good edge coverage.

HIGH SOLIDS COATINGS - CURRENT DEVELOPMENTS

Following the development of higher solids solvent based zinc silicates in the United States, these formulations are now also introduced in Europe. Recent developments in the high solids coatings in Europe are the modification of high build epoxy coatings with glass flakes and the change from polyurethane to non-isocyanate topcoats.

With the incorporation of glass flakes, the volume solids content of high build epoxies is slightly increased, while their barrier properties are improved. By the modification of high solids epoxy coatings with glass flakes, they can easily be applied at considerable higher thicknesses per coat.

Forced by the concerns on the health hazards of polyurethane or isocyanate based coatings in U.K. and the Scandinavian countries, these products are now replaced by non-isocyanates such as acrylic modified epoxies as finish coats in these countries. The acrylic modified epoxies have slightly decreased weathering properties, when compared to the acrylic based polyurethane topcoats.

HIGH SOLIDS COATINGS - STATE OF THE ART

Zinc based primers in combination with high solids epoxy coatings and polyurethane topcoats have been the state of the art in corrosion protection and weathering resistance for many years. Through exploring the siloxane chemistry and combining polysiloxanes with organic binder systems, epoxy siloxane hybrid coatings have been developed. These epoxy siloxane hybrid coatings are high solids coatings at a volume solids content of 90%.

By the combination of the inorganic polymeric structure of the polysiloxanes with the organic epoxy binder system, a coating has been developed that combines the corrosion resistance of high build epoxy polymers and exceeds the weatherability of the best aliphatic polyurethane finish coats. This allows the replacement of traditional anti-corrosive systems with three or four coats by a two coat system.

THE POLYSILOXANE CHEMISTRY

The name “siloxane” is based on the Si - O - Si unit as siloxane and has found acceptance in scientific nomenclature. Polysiloxanes are polymers with the silicon - oxygen (Si - O) backbone. Siloxanes are made from monomeric building blocks and can undergo typical reactions. The silicone atom is tetravalent and it depends on the nature of the four substituents if this small monomer unit behaves as a mono-, di-, tri-, or tetra-functional building block in the synthesis of silicone resins.

R	R	R	O - R
|	|	|	|
R - Si - O - R	R - O - Si - O - R	R - O - Si - O - R	R - O - Si - O - R
|	|	|	|
R	R	O - R	O - R
Mono-functional	Di-functional	Tri-functional	Tetra-functional

R = hydrogen, methyl, ethyl, propyl, octyl, phenyl, other organic

OXYSILANE FUNCTIONALITY

The di-functional units are used to build linear chains. These do vary in individual length, and the medium length can be adjusted to the required value by process control. Introducing tri- or tetra-functional units into the chains gives them the ability for cross linking. The mono-functional units are used as end-cappers, i.e. they can transform reactive into un-reactive groups at the end of along the chain of a resin, or this can be already done with the monomer units.

As shown below, siloxanes are produced from alkoxide silanes by hydrolytic poly-condensation to polymers with an inorganic backbone:

```
  |                        |
- Si - O - R + H2O  ↔   - Si - OH + ROH
  |                        |

    |                  |        |
2 - Si - OH    →     - Si - O - Si - + H2O
    |                  |        |
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$$-Si-O-R + H_2O \leftrightarrow -Si-OH + ROH$$

$$2-Si-OH \rightarrow -Si-O-Si- + H_2O$$

Hydrolysis of alkoxide silanes to produce siloxanes

Not only the number, but also the nature of the reactive and un-reactive substituent in the monomer units can vary, and this variation gives the resins made from these different monomer units, or mixtures of these, their special properties.

Organic substituents can consist of methyl, ethyl, propyl, octyl, phenyl or other organic groups. By the selection of these substituents it is possible to design polymers with varying degrees of hardness and toughness, flexibility, curing rate and secondary reactivity to form interpenetrating networks.

If alkoxide silanes with more than one alkoxide group are used, polysiloxane polymers are produced which can be represented by the generalized structure of a polysiloxane polymer.

```
      R        R        R        R
      |        |        |        |
- O - Si - O - Si - O - Si - O - Si - O -
      |        |        |        |
      O-R      R        R        R
```

The polymeric structure of polysiloxanes differ from the silicone modified organic binders by the typical silicon-oxygen bond as the repeating backbone of siloxane polymers.

To understand the performance difference of organic and inorganic products, the chemical properties of the binders are compared. The high silicon-oxygen bond strength of 445 kJ/mol of polysiloxane binders is stronger than the typical bond strength of 358 kJ/mol for the carbon- bond of organic binders. This means that more activation energy is required to break- down the polysiloxane polymer. Consequently the polysiloxanes are inherently more resistant to atmospheric or chemical break-down.

Inorganic silicon-oxygen bonds are unaffected by sunlight and ultraviolet attack. By comparison organic binders such as epoxies and alkyds typically show early chalking and fading and polyurethanes and acrylics will show fading and gloss loss in a 3-5 year period. Since Si-O is already oxidized, polymers based on such a backbone are not affected by atmosphere oxygen and most oxidising chemicals. In contrast, organic polymers will eventually oxidize and degrade. An inorganic structure is not combustible, organic polymers will burn and generate smoke and toxic fumes.

The siloxanes have very low viscosities allowing the formulation of coatings with very high solids and low VOC's. Siloxanes provide the mechanism to formulate topcoats with excellent gloss and colour retention without the need to use isocyanates for curing.

POLYSILOXANE COATINGS

Through exploring the siloxane chemistry pure polysiloxane network compositions have been developed offering extended weathering and appearance retention, and formulations with maximized thermal and chemical resistance.

By combining organic binders with siloxane polymers, the properties of the traditional resins have been selectively and significantly upgraded. The versatility of the siloxane chemistry, as shown in figures 1, enables the construction of polysiloxane hybrids with epoxies, vinyls, acrylates, fluorinated and phenol resins.

Figure 1 - Versatility of the polysiloxane chemistry

WEATHERABLE EPOXY SILOXANE COATINGS

The novel chemistry achieved by the chemical combination of epoxies with polysiloxanes results in a group of epoxy siloxane hybrids whose unique physical characteristics allow their use as durable binders for the protective coatings industry.

Variation of the types of epoxy binder systems and the pendant organic groups of the siloxanes provide the design parameters for specific coating performance characteristics.

Epoxy siloxane polymers have properties of both the organic and the inorganic resins. The shift in either direction is controlled by the epoxy to siloxane ratio and the types of the epoxy and siloxane resins used.

With the epoxy siloxane hybrid coating, the advantages of the epoxy is combined with the strength of the polysiloxane providing a two component ambient curing thermosetting coating. The quality and durability of the epoxy siloxane hybrid coating is demonstrated by the excellent performance of a two coat epoxy siloxane based coating system in comparison with three and four coat systems of traditional coating systems in accelerated corrosion testing such as salt spray and water condensation exposure tests.

A two coat siloxane system consisting of a zinc based primer and an epoxy siloxane topcoat at a total dry film thickness of 200 µm, tested in salt spray resistance by Battelle, USA for 10.000 hours showed excellent results. 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, electro chemical 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 performed better than any other coating system tested.

The coating system consisting of one coat of a zinc rich epoxy primer at 75 µm and one coat of the high solids epoxy siloxane hybrid coating 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..

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.

Coating systems made with the epoxy siloxane hybrid coatings have been evaluated for gloss and colour retention through accelerated weathering via QUV testing and South Florida marine exposure. Gloss and colour retention are two of many factors that help describe the weatherability of a coating and its ability to withstand weather related effects such as sunlight, humidity, wind and temperature. The qualitative comparison of gloss and colour retention showed that the epoxy siloxane based coating outperformed the best polyurethane based coating system.

Figure 2 offers a comparison of the accelerated UV resistance of the epoxy siloxane hybrid coating in comparison to typical aliphatic polyurethane topocats and an epoxy.

Figure 2

The weathering resistance of the epoxy siloxane hybrid coating has also been tested by the South Florida Marine exposure under an angle of 45 degrees, facing east. After 18 months exposure the epoxy siloxane hybrid coating showed a gloss retention of 90%.

The excellent wetting and chemical bonding obtained with the hydroxy functionality of the epoxy siloxane hybrid coatings has shown in improved adhesion characteristics of this new class of binders. Compared to epoxies, which usually have pull-off adhesion values of 50-70 kg/cm^2 with the epoxy siloxane coating a pull-off adhesion to a blast cleaned steel surface of 190 kg/cm^2 is achieved.

The abrasion resistance of coatings can be determined by testing with the Taber Abrasor following ASTM D 4060. The abrasion resistance of the epoxy polysiloxane is much higher than a typical epoxy coating and even outperforms a polyurethane as is shown in table 3.

System	Abrasion (ASTM D 4060) 1 kg load / 1000 cycles / CS 17 wheel
Epoxy siloxane	53 mg loss
Typical epoxy	102 mg loss
Aliphatic polyurethane	60 mg loss

Table 3 - Comparison abrasion resistance of epoxy siloxane with epoxy and polyurethane coatings

The chemical resistance of epoxy siloxane coatings is superior to both a typical epoxy and also a typical polyurethane coating. A comparison in chemical resistance between these coating systems is shown in table 4.

Chemical	Epoxy siloxane	Epoxy	Polyurethane
Sodium hydroxide 50%	10	10	10
Ammonium hydroxide, conc.	10	0	0
Hydrochloric acid, conc.	10	0	8
Sulphuric acid 93%	6	0	0
Phosphoric acid, conc.	10	8	8
Acetic acid, conc.	0	0	0
Phenol	8	0	0
Acetone	10	10	10
Ethyl alcohol	10	10	10

10 = no change **0 = complete failure**

Table 4 - Comparison of the chemical resistance of epoxy siloxane with conventional epoxy and polyurethane coatings (24 hours exposure)

The very low viscosity of the polysiloxane resin system allows the design of epoxy siloxane hybrids coatings at very high solids. The epoxy siloxane coating is formulated at a volume solids of 90% and a VOC of 120 g/l (EPA method 24) and can be applied by standard airless and conventional spray, roller or brush. It can be applied at a dry film thickness of 75 up to 200 µm, generally without additional thinner.
With the development and use of this high solids two component epoxy siloxane coating system, a considerable reduction in the emission of organic solvents can be achieved.

FIELD EXPERIENCE

The high solids epoxy siloxane coating is in service in various applications, including storage tank exteriors, offshore platforms, bridges, exteriors of ships, hopper cars and exteriors of railway coaches, both in USA and Europe.

During 1994 the 70 year old Peace Bridge, which crosses the Niagara River between Buffalo NY and Fort Erie, Ontario, the bridge has been recoated with a two coat system consisting of a zinc epoxy primer and the epoxy siloxane topcoat as a cost effective alternative to traditional three coat systems. The same epoxy siloxane system has been selected for the protection of the British Gas Armada offshore new building in 1996.

The epoxy siloxane coating, selected as high solids low VOC coating with excellent gloss and colour retention on the exteriors of railway coaches by the Norwegian Railways. The epoxy siloxane coating provided also excellent anti graffiti and dirt repellent properties. After cleaning the coaches from graffiti no shadow of the graffiti or change in gloss could be noticed.

COST SAVINGS

The improvements of important performance categories of the epoxy polysiloxane hybrids as obtained amongst others with their improved weathering in comparison to polyurethanes, their excellent corrosion resistance and their inherent compatibility have offered the possibility to reduce the number of coats in protective coating systems.
This has lead to the elimination of one coat in zinc silicate and zinc epoxy based coating systems where appearance and chemical protection of the zinc primer are requried. In the traditional coating system, an epoxy midcoat is applied for corrosion control and compatibility with the zinc primer and polyurethanes for appearance and weatherability.

With the excellent barrier properties, appearance, weatherability and compatibility of the epoxy polysiloxane hybrid coating, the traditional high performance three coat zinc primer/epoxy/ polyurethane coating system can be replaced by the two coat zinc primer/epoxy siloxane system with significant savings in applied cost.

With the introduction of the epoxy siloxane hybrid coating the CRINE initiative is embraced. The CRINE initiative which stands for Cost Reduction In the New Era, is developed in the U.K. as a drive to reduce development and life cycle cost of capital investments in the offshore industry. A comparison of projected longetivity 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 5.

Based on the NACE publication - *A review and update of the paint and coatings cost and selection guide - NACE Corrosion Conference 1993* (ref 7), and the coating system life project requirements as included in Shell engineering reference document standard (ref 8) CRINE new construction life projections of the three coating systems was calculated at 15 years.

Comparison of projected longevity figures - based on NACE published figures:

Product	Dft, µm	Longevity factor	Sea Coast marine life projections (practical time to repainting 5 to 10% coating break-down)	Offshore life projections (years) (practical time to repainting 5 to 10% coating break-down)	CRINE new construciton life projections
System 1 Blast to SA 2.5					
Zinc rich epoxy primer	75	0.080	6.0	4.0	
1st high build epoxy	125	0.090	11.3	7.5	
2nd high build epoxy	125	0.030	3.8	2.5	
Polyurethane/epoxy acrylic	50	0.030	1.5	1.0	
	375		22.5	15.0	15
System 2 Blast to SA 2.5					
Zinc rich epoxy primer	75	0.080	6.0	4.0	
Epoxy siloxane	125	0.130	16.3	10.9	
	200		22.3	14.9	15
System 3 Blast to SA 2.5					
Epoxy primer	75	0.030	2.3	1.5	
Glass flake	350		18.6	12.4	
Polyurethane/epoxy acyrlic	50	0.030	1.5	1.0	
	475		22.3	14.9	15

Table 5 - Offshore coating systems life projections new construction - practical time to repainting

Explanation
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 longevity project requirement has 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 U.K. Pounds Sterling is reviewed.

By the introducton of the epoxy polysiloxane based system a cost saving of £ 2.35/m^2 in comparison to a traditional four coat offshore coating system and of £ 2.13/m^2 in comparison to a glass flake high solids epoxy system can be achieved (see table 6).

		Zinc epoxy primer Epoxy Epoxy Epoxy /Pu (in µm)	Epoxy polysiloxane over Organic zinc rich Epoxy or IOZ primer (in µm)	ZP primer Glass Flake High Solids Epoxy Epoxy/Pu (in µm)
System	Primer Mid coats Topcoat	1 x 75 2 x 125 1 x 50	1 x 75 1 x 125	1 x 75 1 x 350 1 x 50
Labour cost	Hrs/m^2 £/m^2	0.66 8.18	0.48 5.95	0.60 7.44
Material cost £/m^2	Equipment Grit Gas Coating	2.31 4.00 4.27	1.68 4.00 4.78	2.10 4.00 5.00
Total system cost	£/m^2	18.76	16.41	18.54

Table 6 - Estimated applied cost of offshore coating systems

With the introduction of the two coat epoxy polysiloxane based system in the offshore industry and used by British Gas for the Armada offshore newbuilding, extensive cost savings could be achieved. The Armada project team reported *"This new epoxy polysiloxane based coating system developed and patented by Ameron enables the zinc primer to be protected by a single topcoat of an innovative new polysiloxane paint which combines the advantages of organics and silicones in a single polymer chain. The results are reductions in application time (600 hr/tonne), overspray, platform weight (30% weight of paint saved) and a much simplified maintenance* *regime offshore. In addition the reduced number of coats and overspray results in 70% less solvent emission to atmosphere."*

CONCLUSION

The selection of suitable coating system to protect steel and concrete is becoming more complex. Important integral factors to select the most suitable coating systems must include performance characteristics, efficiency in cost and application, environmental impact, future maintenance and regard to eventual disposal of removed coatings some time in the future.

Using the versatility of the polysiloxane chemistry high performance high solids epoxy siloxane hybrid binder coatings have been developed that comply with the most stringent regulations both in Europe and USA. With a volume solids content of 90% and a VOC or solvent content of 120 g/l (EPA method 24) the epoxy siloxane hybrid coating has a significant lower VOC than all current or planned regulatory requirements in US or Europe.

With the development of the epoxy siloxane hybrid binder systems weatherable coating systems have been introduced with excellent corrosion resistance, extended gloss and colour retention. With these high solids epoxy siloxane coatings, polyurethane topcoats can be eliminated in anti-corrosive coating systems with fewer coats and without the concerns related to the toxicity of isocyanate curing systems. With the introduction of the epoxy siloxane coating the CRINE initiative is embraced, combining excellent corrosion protection at lower applied cost, increased productivity and significant reductions in solvent emission and waste.

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