

# RECENT ADVANCES IN POLYSILOXANE COATINGS

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**SUMMARY:** This publication briefly describes the performance and mechanical property attributes of a newly patented Polysiloxane Technology. The technology manifests itself as a low VOC, rapid curing technology, curing quickly at VOC's as low as 120 g/l. Two technologies of differing VOC's are described in this paper, one at 120 g/l and the other at 420 g/l. These technologies have been compared and contrasted with conventional, non compliant Polyurethane and NISO Technologies.

**Keywords:** Polysiloxane, VOC, Durability, Rapid Cure, Isocyanate Free

## 1. INTRODUCTION:

Polysiloxane coatings (1) are unique class of coating as they offer the coatings formulator some outstanding attributes, some of the key features of this technology are:

- i) Extremely low VOC (as low as 100 g/L depending upon the formulation route taken).
- ii) Outstanding (breakthrough) colour and gloss retention (again dependant upon the unique blend of inorganic-organic resin componentry utilised).
- iii) Extremely good abrasion, dirt pickup and graffiti resistance properties (again formulation dependant).
- iv) Better corrosion resistance at lower dft's when used in combination with Inorganic Zinc, Epoxy Zinc and surface tolerant Epoxies.

Most polysiloxane technology is based on 2K chemistry but 1K siloxane coatings can be formulated as well. Ameron originally developed its siloxane technology (Epoxy Siloxane) for structural steel and concrete to replace the conventional 3 Coat Coating system (2 epoxy coats/1 P/U coat). The advantages of siloxane chemistry are well documented, and as Ameron has pioneered in this area there exists a wealth of literature for the interested reader to delve into (1). This paper discusses some new generation polysiloxane coatings which have been developed with the OEM and new projects markets in mind. OEM and new project markets, of course, have differing requirements to the Maintenance/PC/Marine area- namely rapid cure speeds and improved flexibility. This new siloxane chemistry has been compared with conventional urethane and NISO (Acrylic/Acrylic or Acylic/Epoxy) technologies. Mechanical property attainment, durability (real world and laboratory), corrosion resistance and an environmental perspective relating to the VOC's that can be attained through formulation of IPN siloxane chemistries will be presented.

Polyurethane coatings have been offered up as the doyen of coatings on a global basis for many, many generations. This is because polyurethanes offer an excellent all around range of properties to the applicator, architect and specifier alike. However, in recent years polyurethane coatings have come under a health and safety cloud as this technology has issues with worker safety (respiratory sensitisation) and compliance (dropping below 250 g/l in VOC is an extremely difficult task for this technology). Polysiloxanes, as we will see from this paper may offer a solution as a safer, more durable, faster drying and lower VOC technology.

## 2. THE WORLD, GREENHOUSE GASES, VOC EMISSIONS AND THE FUTURE

The need to conserve energy is no more apparent than when one looks to the language used in the preamble to the Kyoto protocol and also continued pressure on fuel and gas prices. To state the obvious, burning fossil fuels for energy generation creates greenhouse gases, including of course CO<sub>2</sub>. (2) Unfortunately, greenhouse gases have a lifespan in the stratosphere of many hundreds of years, thus generation of greenhouse gases is a problem which will have ramifications for many generations. From a coatings perspective then the message is simple- develop coatings with long lifetimes to first maintenance, that contain low levels of solvent (to reduce generation of tropospheric low level ozone/smog) and that do not need external heat sources to cure them.

The need to reduce VOC has meant that most formulations have focused on:

- i) waterborne coatings
- ii) solvent free coatings (eg polysiloxane variants)
- iii) powder coatings
- iv) UV and/or hot melt technologies

Each of these chemistries has its own problems but in general liquid, ambient cure technologies generally use low molecular weight, highly functionalised diluents which generally create durability problems for the formulator/ end user.

Polysiloxane coatings offer a unique 'fix' to this problem as highly skilled organic chemists have been able to hybridize low viscosity organic polymers with solvent free silicon functional diluents and oligomers. This paper will focus on some properties and attributes of a new generation of siloxane coatings which have rapid cure, excellent corrosion resistance, low VOC and extreme durability. This dissertation will compare and contrast the properties of this class of coatings with conventional coatings and other siloxane coatings which are present in the marketplace.

## 3. WHY ARE SILOXANE COATINGS UNIQUE?

The energy content of one mole (one quanta) of UV light is sufficient to destroy the covalent bonding network prevalent in most polymeric materials. Free radicals are generated by the photophysical processes of adsorbed UV light. The nett result is generation of hydroperoxides and peroxides i.e. the polymer ends up being photo oxidized (Refer Scheme One). (3)

### Initiation step



### Propagation step



### Termination step





## Scheme One: Photooxidation induced by UV light

The combined effects of photolysis and photooxidation of polymers leads to chain scission and/or crosslinking reaction of the UV degraded polymer. The nett effect of these processes is obvious to all coatings chemists i.e. chalking, cracking, checking, reduction in tensile and mechanical property strength and change in glass transition temperature. In simple words the coating fails.

Silicon based polymers are uniquely resistant to photolysis and photo oxidation. This can easily be rationalized when one considers that:

- i) The Si-O bond is already oxidized in an oxidized state and unlike Carbon-Carbon bonds cannot be oxidized further.
- ii) The bond strength or bond dissociation energy for a C-C bond is 145 Kcal/mole cf. a Si-O bond which is 193.5 Kcal/mole (measured at 298K) (4)

In addition siloxane chemistry is also extremely resistant to thermal oxidation reactions to use an analogy one needs only to look at the chemistry of everyday glass (a giant siloxane polymer network). Glass for example melts at 1400°C and upon cooling yields an extremely chemically resistant and thermally resistant material. To use a coatings analogy one could utilize common inorganic zinc or heat resistant siloxane coatings which are capable of providing long term heat resistance at 760°C or greater.

#### 4. GLOSS RETENTION OF SILOXANE COATINGS cf. ORGANIC COATINGS

Figure one details the gloss retention (60 degree) and colour retention of a good quality polyurethane coating, two commonly used NISO coatings, an epoxy siloxane (VOC 120 g/L) and a new generation rapid cure siloxane coating. This data is 'real data' as transcribed from the Allunga exposure station in Northern Queensland.

The % gloss retention data of a coating tabulated after exposure to atmospheric UV light is an indication of the coatings resilience to thermal and/or photooxidative degradation reactions (as described above). White pigmented coatings are traditionally chosen for testing purposes as white pigmentation (rutile TiO<sub>2</sub>) upon absorption of UV light converts oxygen to superoxide and hydroxide ions to hydroxyl radicals. The photoactivity of TiO<sub>2</sub> is thus used by coatings chemists to further accelerate the UV induced degradation of the polymers under test. QUV data has been used by many coatings chemists to simulate what would happen to a coating in the 'real world'. Many papers have been published on this subject, whilst QUV studies offer a comparative guide to exterior performance they cannot replicate 'real data'. As we will see from this study QUV B is NOT a good indicator of real world performance (refer to the gloss retention data extracted from 5 degrees North , Allunga and QUV B studies for the New Generation 420 g/l Siloxane. <refer Figures 1 and 2>).

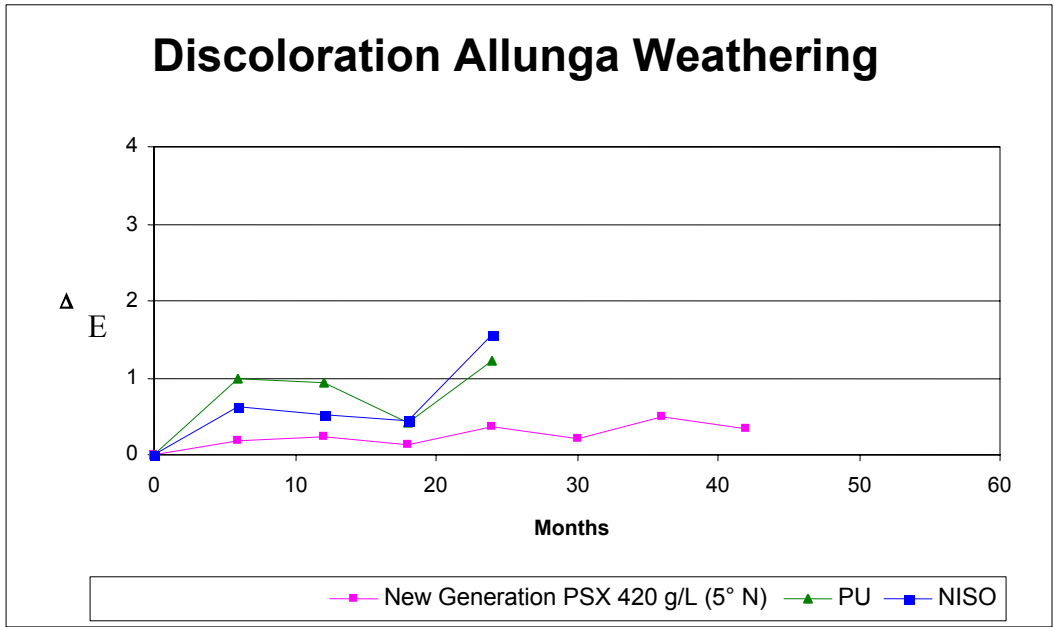
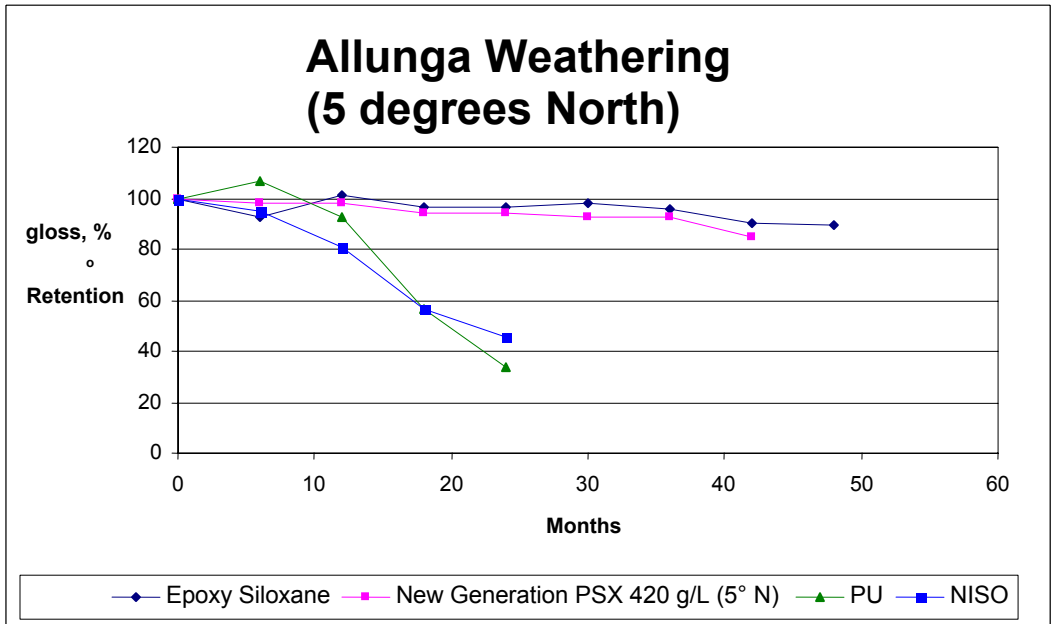


Figure one: 'Real data' – Gloss/ colour retention data from Allunga exposure site northern queensland.

Figure two details the % gloss retention of the same coatings as experimentally determined in QUV studies.

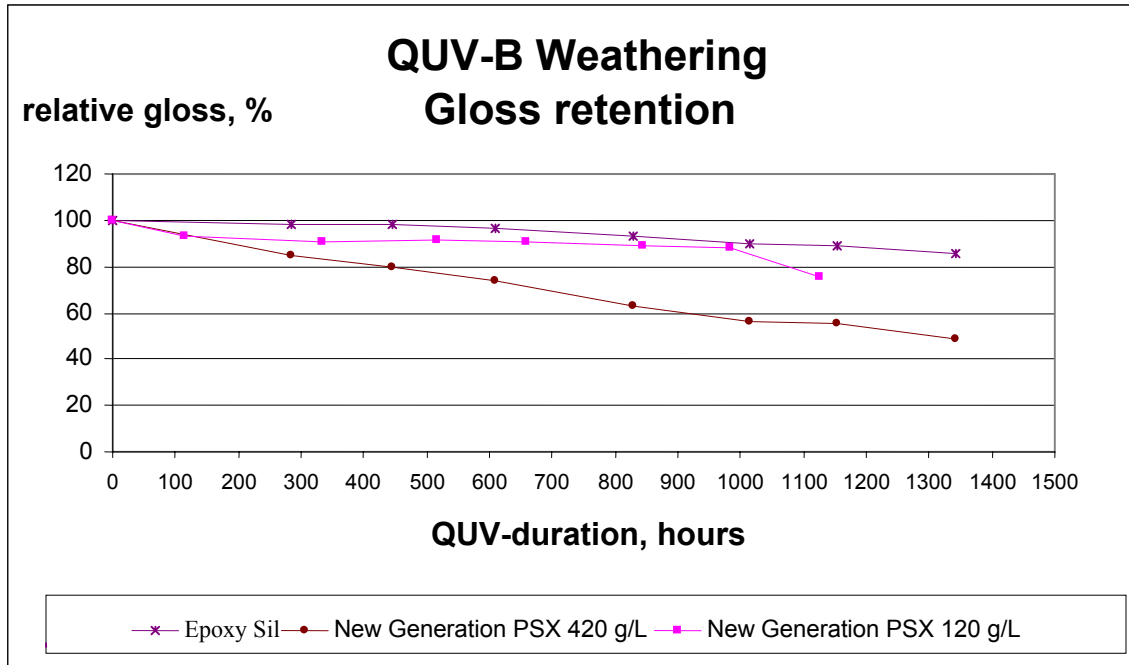


Figure two comparative QUV-B (ASTM G53) gloss retention studies for polyurethane/NISO/PSX700 and new generation siloxane coatings.

The data detailed in figure two illustrates the excellent gloss retention and resilience of polysiloxane coatings to UV induced photooxidation degradation.

**5. MECHANICAL PROPERTY DEVELOPMENT AND ELUCIDATION**

It is necessary for the coatings chemist to develop an appreciation of the internal stress (shrinkage) that develops within a coating as it internally crosslinks and loses solvent. The development of too much internal stress within the coating can cause it to overcome the adhesive strength of the coating system at the primer/topcoat interface and in doing so the topcoat can rip itself away from the primer and/or delaminates or crack. (5) For siloxane coatings, the development of internal strain is generally acknowledged to be related to ‘post cure’ of silanol condensation reactions, thus generating Si-O-Si linkages with elimination of water. Two simple tests which are used to elucidate adhesion and flexibility (and indirectly internal coating stress) are Conical Mandrel (ASTM D522) and Reverse Impact (ASTM D2794) tests. These tests are simple to execute and are reproducible.

Table One details some mechanical property attributes for a number coatings as evaluated immediately and after post curing for various period of time.

Property	Test Method	New Generation Siloxane (120 g/l)*	Acrylic Polyurethane (530 g/l)	NISO Acrylic/Acrylic 2K system (530 g/l)
Conical Mandrel Flexibility	ASTM D2794	18%	24.3%	17.3%
Impact Resistance	ASTM D522	6J	4J	3J

Table one: mechanical property attainment of various coatings.

\*Coating had been aged for 2 months in a 60 degree oven with ca. 85% humidity to fully elucidate mechanical properties as expected in real service life conditions

The results of table one indicate that new generation siloxane coatings can be formulated to provide excellent conical mandrel and impact resistance . More sophisticated testing on the development and understanding of internal stress buildup within this technology is underway and will be reported upon in future publications.

**6. CURE SPEED ATTRIBUTES OF NEW SILOXANE TECHNOLOGIES**

The attainment of rapid cure (that is the ability of the fabricator to be able to handle and ship coated parts at short time intervals after painting) for coatings is one of the most difficult challenges that faces the coatings chemists especially when one is formulating coatings at VOC's approaching that of waterborne coatings (i.e. ca. 100 g/L). More important still is the need to recognize that waterborne coatings will not coalesce under conditions of adverse low temperature and high humidity and as the level of coalescing solvent is dropped to lower VOC the effect of temperature and humidity becomes more pronounced. The need for attainment of minimum film formation temperatures for waterborne coatings is certainly a limitation of emulsion technology even though they are recognized as a true environmental coatings solution.

Dust free, tack free and print free data for a polyurethane, NISO coating and siloxane coatings are shown in figure three , this data was recorded at 17 degrees celcius at a relative humidity of ca. 65%. Table two details the dust free, tack free and print free data for the same coatings except the data was recorded at a temperature of three degrees celcius at a relative humidity of ca. 80 %. Sward rocker hardness is illustrated in figure 5 for the same coatings.

Sward Hardness Development ASTM D2134	New Generation Siloxane (420 g/l)	New Generation Siloxane (120 g/l)*	Epoxy Siloxane (120 g/l)	Acrylic Polyurethane (530 g/l)	NISO Acrylic/Acrylic 2K system (530 g/l)
1 day	18	12	10	26	20
2 days	28	26	20	28	22
3 days	32	34	28	38	34
7 days	32	34	46	44	36
42 days	34	36	54	48	44

Table Two Comparative Sward Rocker Hardness Development for a range of coatings

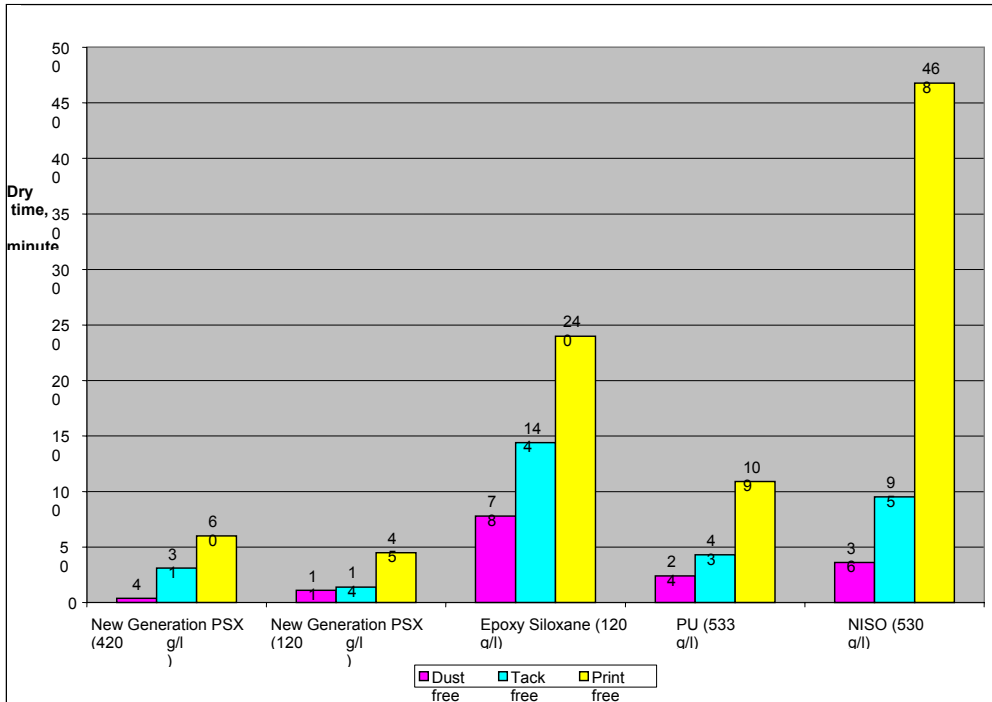


Figure 3: Dust free, tack free and print free attributes of siloxane coatings cf. conventional technologies at 17 degrees Celcius and 65% relative humidity.

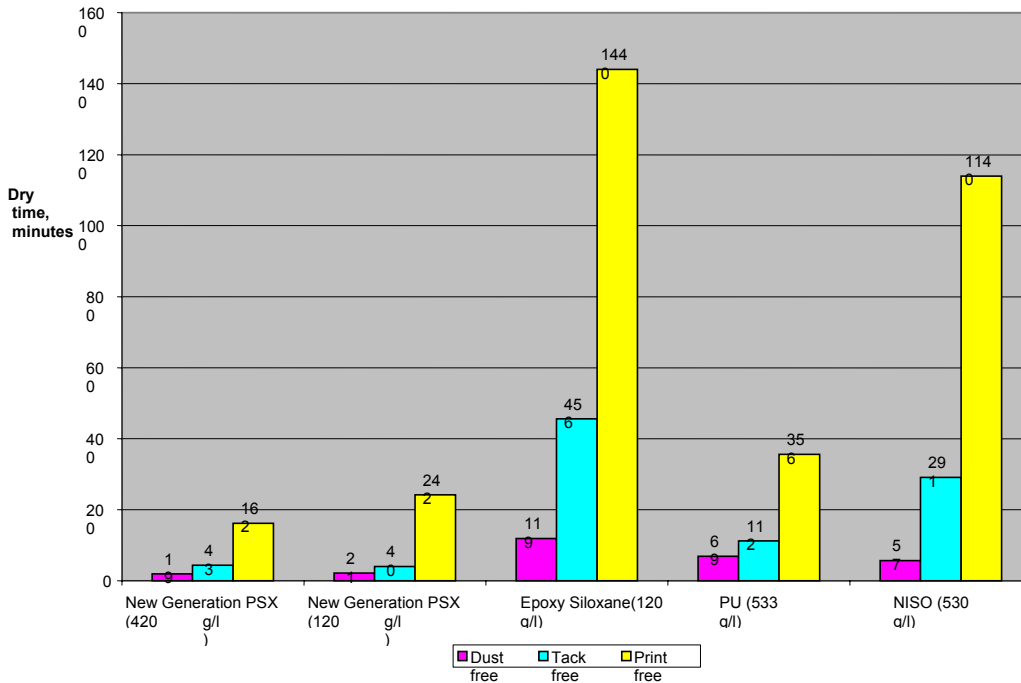


Figure 4: Dust Free, Tack Free and Print Free times for polyurethane, NISO and siloxane coatings as measured at three degrees celcius and a relative humidity of ca. 85%.

**7. SALT SPRAY CORROSION RESISTANCE OF SILOXANE COATINGS cf. CONVENTIONAL TECHNOLOGIES**

Polysiloxane coatings were originally formulated to offer the applicator outstanding corrosion resistance at lower dft's cf. a conventional 3 coat system i.e. epoxy zinc/ epoxy build coating/ PU topcoat. NACE have published data on the service life of various coatings in differing corrosive environments. Extensive test data from natural and long term weathering studies has shown that epoxy zinc/epoxy siloxane systems will conservatively provide a 30% increase in the service life to first maintenance at ca. 20% less total dry film builds cf. a traditional 3 coat system. (1, 6) The interested reader is referred to the wealth of reading material that exists if more detail is needed. This publication simply reinforces Ameron's opinion that properly formulated siloxane coatings offer unique advantages to the end user in terms of life to first maintenance.

Salt Spray Resistance	New Generation Siloxane (120 g/l)	New Generation Siloxane (420 g/l)	Epoxy Siloxane (120 g/l)	Acrylic polyurethane (530 g/l)	NISO Acrylic/ Acrylic 2K (530 g/l)
1000 hrs ASTM B117					
Over Epoxy Mastic					
• Rusting/blistering	10/10	10/10	10/10		
• Scribe blistering/creep	10/9	10/9	10/9	N/A	N/A
Over IOZ					
• Rusting/blistering	10/10	10/10	10/10		
• Scribe blistering/creep	10/9	10/10	10/10		
Over Epoxy Zinc					
• Rusting/blistering	10/10	10/10	10/10		
• Scribe blistering/creep	10/9	10/9	10/9		
Cleveland Humidity, 1000 hrs ASTM D2247					
Over Epoxy Mastic	10/9	10/10	10/9	N/A	N/A
Over IOZ	10/10	10/10	10/10		
Over Epoxy Zinc	10/10	10/10	10/10		

Table 3: Salt spray resistance (ASTM B117) and humidity resistance (ASTM D2247) of new generation siloxane coatings over inorganic zinc, zinc epoxy and epoxy zinc primers .

**8. CHEMICAL RESISTANCE AND PULL OFF ADHESION OF NEW GENERATION SILOXANE COATINGS OVER PRIMERS**

The chemical resistance and crosslink density of this class of siloxane coatings has been detailed in table four. The data is unexceptional and illustrates the good all around chemical resistance of the new class of siloxane coatings technology (1)

Coating system	New Generation Siloxane (420 g/l)	New Generation Siloxane (120 g/l)	Epoxy Siloxane (120 g/l)	Acrylic PU (530 g/l)	NISO Acrylic/Acrylic (530 g/l)
Chemical resistance ASTM D1308 modified					
10% Acetic acid	6	6	8	10	7
50% Sodium Hydroxide	8	6	6	10	10
Conc. Ammonium Hydroxide	10	8	8	10	6
Acetone	10	10	10	0	4
95% Ethyl Alcohol	10	10	10	0	4
MEK double rubs (NCCA-II/18)	200+	200+	200+	150	200+
Pull off Adhesion (ASTM D2247) Over Epoxy primer	6 MPa (cohesion failure of primer)	7 MPa (cohesion failure of primer)	7 MPa (cohesion failure of primer)		
Epoxy Zinc	8 MPa (adhesion failure to primer)	6 MPa (cohesion failure of primer)	8 MPa (cohesive failure of topcoat)		

Table four. Delineation of crosslink density, chemical resistance of pull off adhesion from common primers used in the heavy duty and marine markets.

## 9. CONCLUSIONS

This paper has briefly touched on some new research initiatives to design 2K siloxane coatings which cure quickly at low and ambient temperature. These coatings have been designed primarily for the Industrial and OEM markets. The test data on these new siloxane coatings is truly exciting when one realizes that VOC's of 120 g/l can be attained whilst not losing any of the conventional properties of siloxane technology. That is excellent gloss and colour retention, excellent corrosion resistance, good chemical resistance and adhesion to conventional primer technologies such as epoxy zinc, inorganic zinc and surface tolerant epoxy products. This publication has shown that it is possible to formulate siloxane coatings with 'breakthrough' performance attributes but with the added advantages of rapid cure (at ambient and low temperature) and excellent flexibility attainment. More research into this "eco friendly" technology is underway and as such will be subject to more patents and publications

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