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Silicon and nitrogen

A new class of inorganic or hybrid organic/inorganic polymers called polysilazanes with silicon-nitrogen (SiN) linkages in the polymer backbone has been developed. Upon pyrolysis they form ceramics, but even curing at normal stoving or ambient temperatures can provide high performance coatings. Their use to protect against graffiti, corrosion and weathering is reviewed.

Polysilazanes produce thin-film easy-to-clean and anticorrosive finishes

A new class of polymers with silicon-nitrogen (SiN) linkages in the polymer backbone has been developed. These polysilazanes can be considered either as inorganic polymers ("perhydropolysilazanes") when the side groups are all hydrogen, or organic polymers ("organo-polysilazanes") when the side groups contain carbon. They are useful both as ceramic precursors and to produce coatings having high mechanical durability and thermal performance. The coatings have excellent adhesion to polar substrates (glass, plastics, composites and metals) thanks to the strong bonding of reactive SiH and NH groups at the surface, and low surface energies, so that easy-to-clean, anti-graffiti characteristics can also be obtained. They also have other very useful properties such as resistance to corrosion and high temperatures.
The chemistry of polysilazane ceramic precursors, their range of applications and several case studies on easy-clean coating applications and corrosion protection in the transport and automotive industries are described below.

Easy-to-clean surfaces are useful in many applications

Easy-clean properties are desirable in many industries. Graffiti on buildings and transport vehicles are costly to remove. Huge sums of money are spent to keep such surfaces clean. Formulated with aggressive solvents, acids and pigments, the graffiti adheres strongly to both walls and railway paints, making removal difficult. Strong cleaning solvents are not always effective, and their use can degrade the original surface.
Exterior architectural coatings also suffer from weathering. Outdoor stains and dirt are generally mixtures of organic/ lipophilic and inorganic/hydrophilic compounds originating from car exhaust and construction projects. These mixtures, once deposited, stick tenaciously and are very hard to remove.
Wood and plastic articles used in house construction and flooring also suffer from staining caused by tar and ashes. Metals such as bronze, steel, aluminium and copper, as well as the silicon wafers used in microelectronic applications, and exhaust manifolds, pistons and cylinders used in vehicle engines all suffer from thermal and chemical corrosion.
Proposed solutions to these problems vary from creating a repellent hydrophobic surface effect using fluorosilanes or silicones to the creation of hydrophilic surfaces with photocatalytic effects produced by anatase TiO_2 to decompose organic stains. Hydrophobic surface structuring (the "Lotus-effect") is also advocated as a way to prevent the adhesion of dirt and ease its removal by water washing.
Coatings also often require other properties to ensure their long term durability: resistance to light, temperature, abrasion, chemicals, mechanical stresses, and temperature.

Basic chemistry of polysilazanes

A variety of oligomers and polymers of polysilazanes, such as perhydropolysilazane (PHPS), polymethyl(hydro)silazane (PMS), polymethyl(hydro)/polydimethylsilazane (PMDMS), and polymethyl(hydro)/polymethylvinylsilazane (PMVS), are available commercially. Their structures are shown in Figure 1. These can be modified by the introduction of various organic or inorganic functional groups, resulting in a broader range of products with properties which can be adapted to many applications.

Several possible curing mechanisms

Whereas PHPS needs thermal curing, various organopolysilazanes can be cured in air at ambient temperature. The cure mechanism proceeds through moisture-induced crosslinking promoted by humidity. The cure rate is enhanced by increasing relative humidity and temperature [1].
PHPS reacts through hydrolysis/condensation reactions to form dense SiO_2 as shown in Figure 2. This conversion can be followed by ATR/IR (Attenuated Total Reflection/Infra-Red) spectroscopy with the disappearance of SiH (2170 cm1) and NH (3380 and 1180 cm1) absorbances and the formation of SiOSi (1040 cm1) bond schemes. Metal and amine catalysts can accelerate the kinetics of curing.
The organopolysilazanes PMS or PMDMS react similarly. ATR/IR analysis shows that the cure condensation reaction is slower than PHPS due to the presence of organofunctional groups.
Materials such as PMVS readily polymerize with heat, by radical initiators or by radiation induced crosslinking (EB/UV).

Thin film coatings with high levels of protection

Reference to many applications of polysilazanes can be found in the literature. The measured pencil hardness of thermally cured PHPS coatings is 7H and indentation measurements indicate hardness values of 2000 N/mm². Such values are far superior to organic polymers such as PC or PMMA, (Hv » 100-200 N/mm²). Due to its reactive SiH and NH bonds, PHPS adheres to most polar substrates, including glass, metals, or plastics and protects them well against scratching, corrosion, thermal oxidation and chemical degradation.
PHPS formulated with hydrophilic promoters demonstrating surface energies of gH2O = 10-20 mN/m has been used to coat painted automotive surfaces and windows. Super-hydrophilic behaviour can be obtained by incorporating TiO_2 nanoparticles. Coatings as thin as 0.5-2 µm are sufficient to ensure good surface protection and keep outdoor housing tiles and car windows clean.

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PHPS is currently used in the electronics industry as a precursor to silica in the manufacture of dense or porous surface coatings on the surface of substrates such as silicon wafers. The coatings are also very effective in protecting anodised aluminium, bronze, steel, copper and other alloys against corrosion. PHPS's exceptional barrier properties to oxygen permeation (0.2 cm3 m² day1 bar1) and to water permeation (1 cm3 m² day1 bar1) are of interest in the packaging industry.

Organic functionality extends application range

The incorporation of organofunctional groups in polysilazanes allows versatile functionalisation of these polymers [2]. PMVS polymers cure to solid materials by heating to 180-200°C or at lower temperatures when using free radical initiators such as dialkyl peroxides, peroxyketal, diperoxyester, alkyl peroxyesters and peroxycarbonates. EB, UV, laser, or microwave radiation can also cure these polymers efficiently.

PMVS polymers are usually used as ceramic precursors to CMC (ceramic matrix composites) which are obtained upon pyrolysis at temperatures of 1000°C or greater under controlled atmospheres, where the polysilazane is transformed either into SiC (silicon carbide) or Si3N4 (silicon nitride) ceramics.

Tough, fire-resistant PMCs (polymer matrix composites) can also be obtained when organopolysilazanes are combined with conventional organic polymers. These PMCs and CMCs are useful in high temperature applications where alternative materials are unacceptable. Applications include components for the aerospace, defence and underbonnet automotive markets as well as in MEMS (microelectromechanical) electronic devices.

PMVS and PMDMS can be formulated with non-oxide ceramic powders (SiC, B4C), metal powders (Al, Cu, Zn) and/or metal oxide powders (ZrO2, SiO2, Al2O3) to design coatings that endure temperatures in excess of 1,000°C in air or corrosive atmospheres without delaminating from metal substrates. Typical applications are heavy duty coatings for high temperature oxidation and chemical resistance in areas including gas turbine engines, aerospace components, high performance motor sport vehicles and metal and glass article manufacturing.

Both ambient and thermal curing possible

Organopolysilazane clearcoats combine oxidation and corrosion resistance with UV stability and high hardness. They will adhere to a wide variety of substrates metal, painted surfaces, glass and polymers and remain clear and colourless at very high temperatures. Four ready-to-use organopolysilazane clearcoat products are currently available:

- A clearcoat and and an anti-graffiti coatings which cure at room temperature. Both products, once applied, are dry-to-touch at ambient temperature within 1 hour of application.
- Acrylic and urethane hybrid clearcoats in the same range which are thermally cured at 150°C. These offer the benefits of an inorganic and an organic polymer combined in a single tough and abrasion resistant coating.

Clearcoats are used in many market areas, such as in the in automotive industry, where they are often used to protect aluminium wheels against corrosion, chipping and yellowing due to "baked in" brake dust. Anti-graffiti clearcoats are used in rail transportation. Decorative aluminium windows and facades are kept clean using anti-graffiti easy-to-clean coatings. Other applications such as traffic signs, bus shelters and aluminium building facades are also currently coated with organopolysilazane clearcoats.

Polysilazanes in the protection of conventional coatings

A range of ready-to-use polysilazane clear coats is available that are very efficient in protecting vehicles against graffiti and are already used by many European railways. Exterior and interior painted components in coaches resist graffiti applied from aggressive markers and spray paints after a 5 µm thick polysilazane coating is applied. Polymer composites, plastics, and metal parts are also protected due to the exceptional adhesion of these coatings on many surfaces.

The low viscosity coating, sprayed or wiped on under ambient conditions, is dry-to-touch after one hour and demonstrates full performance after a few days. The low surface energy (gH2O =105 mN/m) makes the coatings impervious to paint and marker ink, which simply form non-adherent droplets, as shown in Figure 3. Their dense structure blocks any chemical deposits from forming on the surface. Removal is facilitated with the use of simple cleaning solvents.

By railways standards, this is considered a permanent and durable clearcoat which protects well painted parts and decorative adhesives against weathering, cleaning procedures, dirt and graffiti. Recoating and repair are feasible by using various primers or by slight surface abrasion, which allows for overcoating [3].

Exterior paints, if not protected correctly, chalk when exposed to light. Hindered amine light stabilizers (HALS) are often used to limit premature degradation. Figure 4 shows a typical painted surface in use by the German Railway. When this has been further overcoated with a polysilazane clearcoat, it resists 3000 hr of UV radiation (DIN 11341, Xenon test) without chalking or delaminating from the painted surface.

Colour and gloss are maintained along with desirable antigraffiti properties. It is also possible to renovate old, painted vehicles simply by applying this clearcoat to obtain a new glossy appearance.

As a car brake is applied, it liberates very aggressive phenolic dust particles which can adhere strongly to aluminium rims. Protecting the polyester/polyacrylic varnishes which are typically used by overcoating with a polysilazane or polysilazane/polyurethane hybrid clearcoat prevents premature yellowing of the rims.

Figure 5 shows that the gloss and colour of the varnish remains unchanged on contact with hot brake dust at 160°C for 2 hrs when the rim coating is overcoated with a polysilazane clearcoat. Actual in-use testing indicates that rims remain dust-free even after one year of intensive use.

Direct application to metal

Polysilazane clearcoats show very good adhesion to metal surfaces such as aluminium, brass and copper without the need of a primer coating. In Figure 6, the modified filiform test (24 h CASS-test then 1000 h exposure to temperature and humidity) shows no delamination and no propagation of corrosion along or beneath the scratch line.

This shows that SiHNH/metal bonds are very strong ones. This is not the case for polyacrylate or polyester powder coatings. Polysilazanes can, therefore, be thought of as chromate-free adhesion promoters. The mechanism of adhesion, however, needs further study.

Polysilazane clearcoats can be further formulated by adding fillers, pigments and additives to obtain coloured coatings having low surface energy and corrosion resistance. In this example, the resins are mixed with pigments ("Hostaperm" green, blue and black from

Clariant) to produce coatings with multifunctional properties: coloured, easy-to-clean with excellent resistance to weathering. No dimensional change, coating degradation, or loss of properties is observed after 2800 h of exposure to weathering by Xenon Arc testing (DIN 11341) (Figure 7a). The same pigmented coatings, coated directly on aluminium "Q-panels" and cured at room temperature show no chemical corrosion, dimensional change or delamination after 260 hours of salt spray testing to DIN 50021 (Figure 7b).

Polysilazanes offer exceptional versatility

Inorganic and organic polysilazanes are a versatile new class of polymers with backbones featuring SiN bonding. They are best known as precursors for ceramics, but when used as coatings, they offer very good protection for metal and organic substrates against chemical and mechanical attacks. Chemical bonding between the reactive SiH and NH functionalities to polar groups on substrates, along with a dense coating structure, explain the good protection of paints against graffiti and the protection of various metals against corrosion.Polysilazanes can be formulated with dyes and pigments to give coloured coatings retaining these properties. Test results have been presented which show the high potential of polysilazanes as versatile and easy-to-use products in the formulation of novel coatings possessing multifunctional properties.

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REFERENCES

[1] F. Bauer, Prog. Organic Coatings 53 (2005) 183-190
[2] Kion Corporation http://www.kioncorp.com
[3] J. Krüger (Deutsche Bahn), New concepts for durable vehicle surface protection from impact during operation and vandalism, Ecolromat conference, October 2006, Mulhouse (France

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- A new class of polymers with silicon-nitrogen (SiN) linkages in the polymer backbone has been developed. These polysilazanes can be considered as inorganic polymers ("perhydropolysilazanes") when the side groups are all hydrogen, or organic polymers ("organopolysilazanes") when the side groups contain carbon.
- Upon pyrolysis at temperatures in excess of 1,000°C they form ceramics suitable for ultra-high temperature applications. However, even coatings cured at ambient temperatures can offer high mechanical durability and thermal performance.
- Their excellent adhesion to polar substrates and low surface energies make them suitable for easy-clean, anti-graffiti coatings. They also resist corrosion and high temperatures.
- A number of examples are presented, showing the use of these coatings to protect surfaces or conventional coatings from corrosion, weathering and graffiti.

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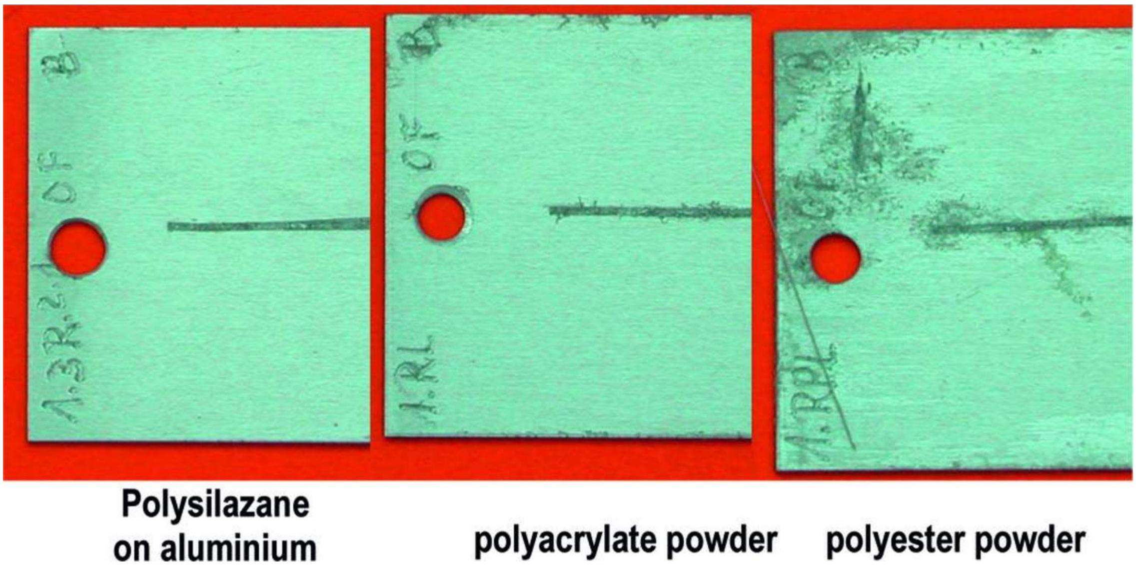

Figure 6: Modified filiform test (24 h CASS-test then 1000 h exposure to temperature and humidity) of polysilazane, polyacrylate and polyester coatings applied directly on aluminium

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Figure 7: Pigmented polysilazane coatings - a) weathering test

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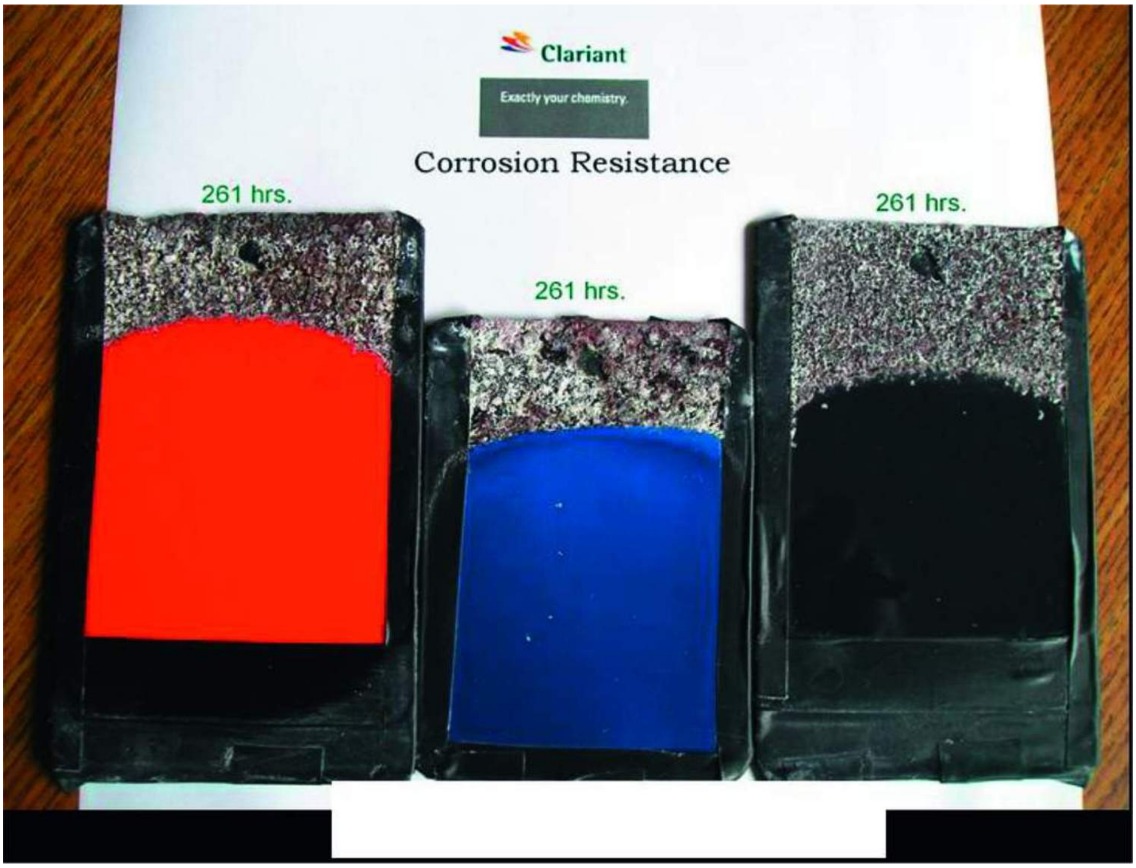

7b) corrosion resistance

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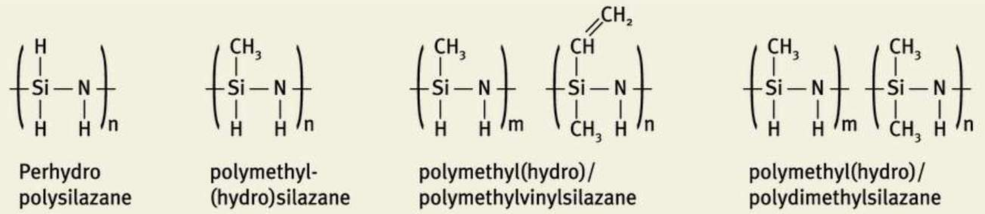

Figure 1: Chemical structure of simple polysilazanes

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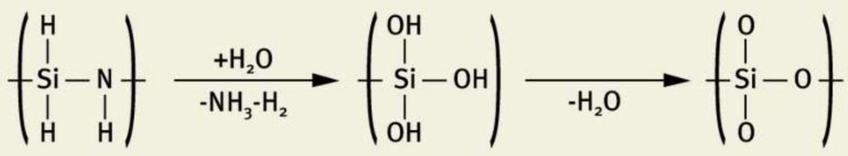

Figure 2: Reaction scheme of PHPS showing formation of silica

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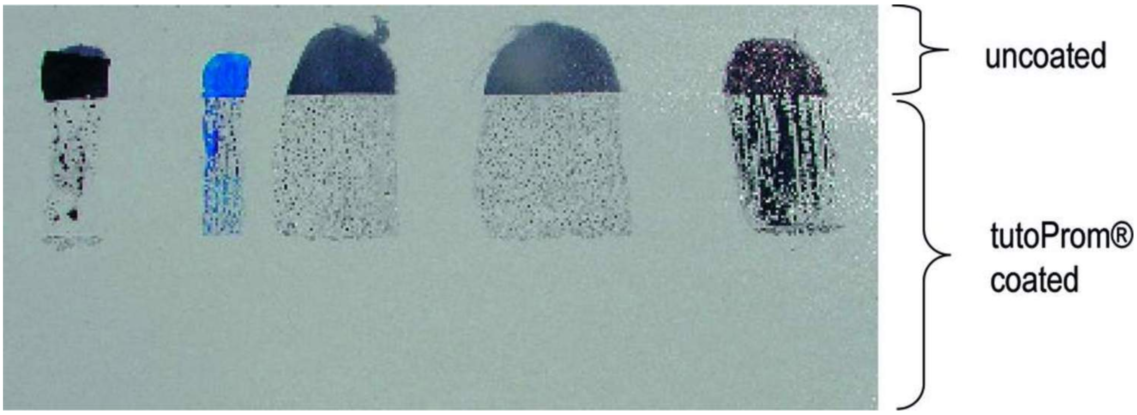

Figure 3: Effect of polysilazane overcoating in improving graffiti resistance of a railway paint

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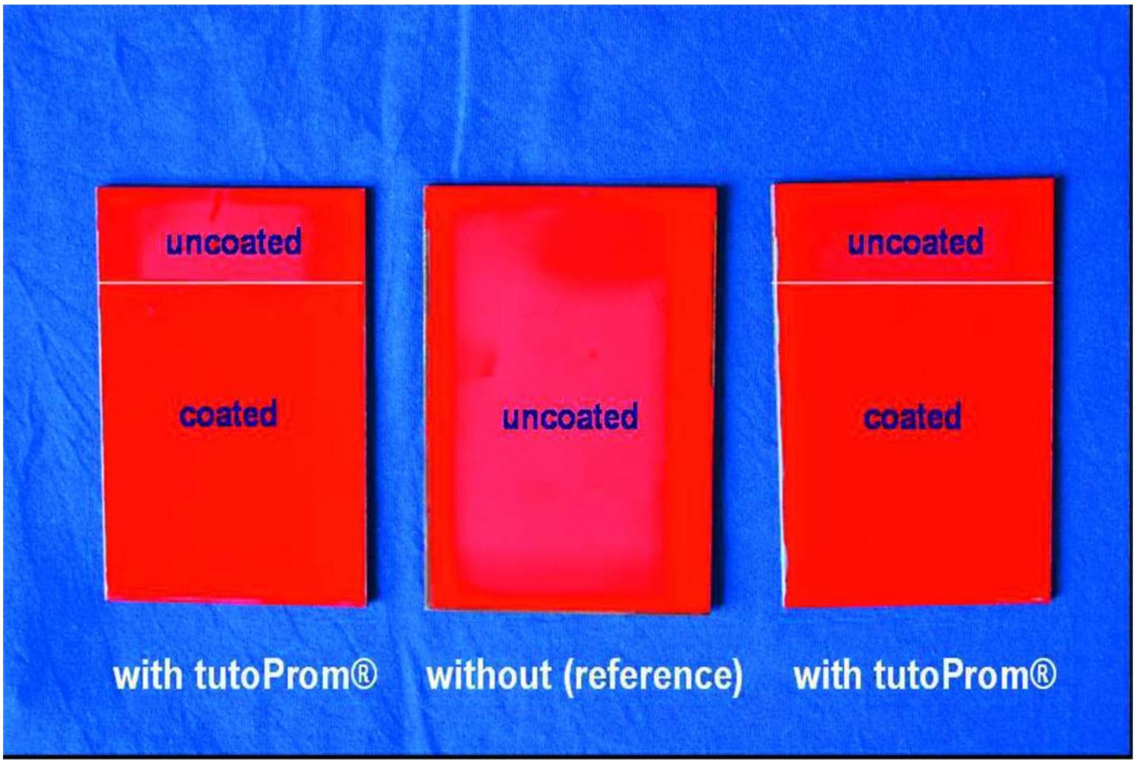

Figure 4: Improvements in weathering resistance obtained by overcoating with polysilazanes

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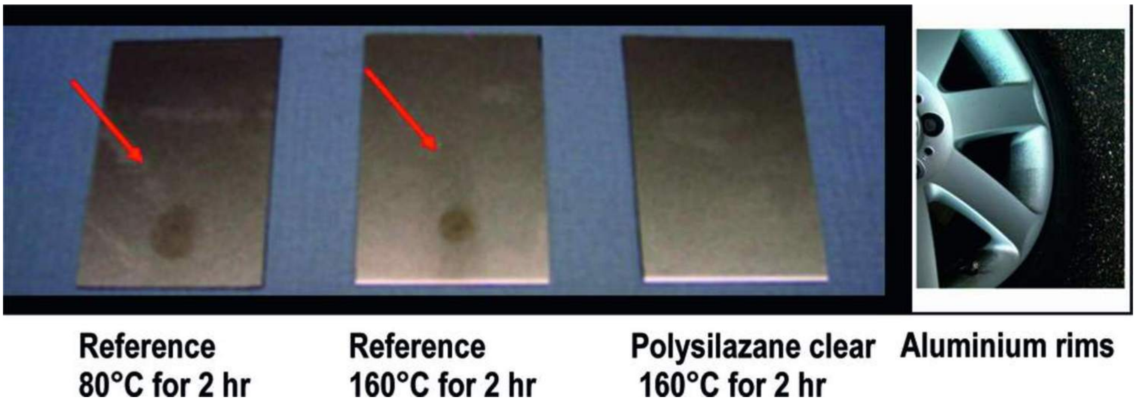

Figure 5: Improvement in resistance to brake dust by applying a polysilazane clearcoat to aluminium wheels