SILANE-BASED CONVERSION COATING FOR METALS

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For the past three years, a project to develop new pretreatment rinses for metals was carried out by the U.S. Environmental Protection Agency and the University of Cincinnati. The project involved optimization of laboratory rinses with dilute aqueous solutions organofunctional silanes. Metals included: cold-rolled steel, electrogalvanized steel, hot-dip galvanized steel, aluminum and its alloys, and Galvalume®. Metals were painted with polyester or polyurethane powder paint systems after silane treatment. It was shown that if properly selected and applied, the silane treatments can outperform the currently used chromating and phosphating systems for these metals. This performance is reported for the salt spray test(ASTM B-117) and for the GM 9540P accelerated cyclic corrosion test(GM scab). This presentation will report on the corrosion performance and other results of the silane-treated metals.

The toxic or carcinogenic properties of chromates have been widely documented in recent years(1). Their use has been banned from many applications. Because of their unique properties, it has not yet been possible to replace chromates (or phosphates with chromate final rinses) with treatments that are universally applicable and cost effective without loss of performance in the corrosion control of painted metals such as cold-rolled steel(CRS) or hot-dip galvanized steel(HDG). Many chromate replacements have been proposed, but none of them is currently widely used except for some niche applications.

Which silanes work on metals? In principal, all functional silanes that are trialkoxy esters can be used on metals. The preferred way of applying them on a metal substrate is to hydrolyze a dilute solution of the silane in water first, typically:

$$\text{X-}CH_2CH_2CH_2\text{-}\ Si(OCH_3)_3 \rightarrow \text{X-}CH_2CH_2CH_2\text{-}\ Si(OH)_3 + 3\ CH_3OH$$

where X is an organofunctional group. The alkoxy groups are, in principle, quantitatively hydrolyzed to active silanol groups. However, if this hydrolysis is not complete, films of good quality can still be formed. The remaining ester groups will then hydrolyze when the treated metal is exposed to air.

Several silanes have been studied at the University of Cincinnati for a number of years. They include: γ-aminopropyl triethoxy silane(γ-APS) and bis-1,2-(triethoxysilyl)ethane (BTSE). Active structures are obtained after hydrolysis with water. Both silanes are supplied as ethoxy esters. The properties of the films obtained by dipping CRS, HDG, and Al(alloys) in the freshly hydrolyzed silane solutions as a function of metal cleaning procedure, concentration of the silane, pH of the solution, and dipping time were determined by a wide range of techniques. An important conclusion of these studies was that in all metal/silane combinations that was studies, it was found that the thickness of the film was determined solely by the concentration of the silane in the aqueous solution and not by the dipping time.

The silanes γ-APS, γ-UPS(γ-ureidopropyltrimethoxysilane), VS(vinyltrimethoxy-silane),SAAPS(styrylaminoethylaminopropryltrimethoxysilane, with low Cl- content) and BTSE were obtained from OSI Specialties Inc. in Tarrytown, New York. They were all used without further purification. These mixtures(10% silanes) were hydrolyzed by stirring for 1-12 hours. They were then diluted to the working strengths and pH-adjusted again.

CRS, HDG and two-sided electrogalvanized steel(EGS) panels of standard quality and dimensions were obtained from ACT in Hillsdale, Michigan. The Galvalume®(GVL) panels were obtained from SSAB in Borläng, Sweden. Before silane treatment all panels were cleaned in the alkaline cleaner Parker 338 for 1-5 min. at 60 °C with the exception of GVL. That metal was cleaned with either Ytex 4324(pickling) or Ytex 4345(mild) from Ytteknik AB, Sweden. Both are alkaline but the pickling(etching) one results in a zinc-rich surface, the other one leaves the surface Al-rich(2).

After alkaline cleaning the panels were rinsed in demineralized water and immediately dipped in the freshly hydrolyzed silane solution at room temperature for 2 min. The film was blown dry with compressed air and some panels were immediately treated in the second silane solution using the same procedure. All silanes were hydrolyzed in water which was pH-adjusted by acetic acid or sodium hydroxide. Hydrolysis times were several hours at room temperature.

Silane treatments were mostly compared with iron phosphate, zinc phosphate, or a chromate system typical of that metal and application. The paints were mostly standard polyester(PE) or polyurethane(PU) powder paints. The tests that were conducted were usually the standard salt spray test (ASTM B-117) and an indoor accelerated cyclic corrosion test(GM scab) for painted metals. The test panels were evaluated by measuring the scribe creep(corrosion propagation from a 45 degree scribe in the paint) or in the case of GVL, the propagation of corrosion from the edge of the panel. In the case of white rust inhibition testing, a stack test was conducted at 60°C and 85% r.h. The filiform corrosion test was a European standard for painted Al panels(1-hour HCL activation followed by exposure in an environment of 40°C and 90% r.h.)

Scribe creep observed in PU-powdered-painted CRS after salt spray and GM scab testing showed the 2-step silane treatment is equivalent or better than the industrial standard phosphate + chromate rinse.

Table 1. Scribe creep in mm in PU-powder painted CRS panels

No.	Treatment of CRS	14 Days GM Scab	25 Days SST*
1	Alkaline-cleaned only	30.0±1.2	51±24
2	Iron Phosphate	14.5±0.8	23.2±0.9
3	Iron Phosphate + Chromate	5.0±0.5	2.2±0.3
4	Optimum silane treatment**	2.5±0.3	2.5±0.5

*salt spray test, ASTM B-117
**2 min dip in 2% BTSE of pH=6 followed by 0.5 min dip in %γ-APS of pH=10.5

Similar experiments with painted EGS were performed. Again the results show the optimized silane treatment provides the same or better performance than the best industrial standard which is a zinc phosphate with a final chromate rinse.

Table 2. Scribe Creep in mm in PE-powder painted EGS

No.	Treatment of EGS	6 weeks GM scab	5 weeks SST
1	Akaline-cleaned only	16.2±5.9	24±19
2	Standard zinc phosphate	3.3±2.0	2.7±0.9
3	Optimum silane treatment*	3.1±2.2	1.3±

*2 min dip in 2% γ-UPS of pH=8

Also tests were performed on powder painted HDG panels. Again, the optimum treatment comprises only one silane and in this case it was a vinyl silane that outperformed.

White rust performance of the VS treated HDG panels show that the silane-treated HDG has a white rust resistance far superior to that of a standard temporary chromate system. Further, such a chromate system has to be removed if the HDG panels are phosphated, e.g. in automotive applications. Therefore, it provides corrosion protection before and after painting and there is no need to remove it prior to painting.

Table 3. White Rust Performance(stack test) of silane-treated HDG

No.	Treatment	Percent White Rust(14 days)
1	Alkaline-cleaned only	100
2	Standard temporary chromate	50
3	5% VS of pH=6(2 min dip)	0

Important in the application of silane process is the type of cleaning used. In general, an aggressive alkaline cleaning works best for most metals. Following cleaning, the silane must be applied as quickly as possible. Results obtained after dipping, spraying, wiping or brushing are identical. After silane treatment, the meal surfaces are practically indefinitely stable i.e. it is not necessary to paint the metal immediately. Exceptions are systems in which γ-APS are used: the amino groups are not stable in the air but oxidize to imine groups with a much lower surface energy.

Summary

In summary, the silane processes are currently the most promising to replace chromates in many metal finishing industries(3-4). Among the major advantages of this process for metal protection are:

- the process is flexible: it can be optimized for the metal and application
- the process and materials appear to be environmentally compliant
- the corrosion performance of treated metals outperforms currently used chromate and phosphate systems

- the treatments can provide excellent corrosion resistance even without paint coatings.
- chemicals are commercially available and relatively inexpensive.
- the treatment involves fewer steps than phosphating, viz., cleaning, dipping, and optionally dipping in a second silane. There are essentially no rinse steps. Drying is at room temperature.
- the 2-step process provides improved adhesion to polymers and paints.
- the 2-step process allows the optimization of the process for a particular polymer or paint system.
- Several different forms of corrosion are improved by the silane treatments; treatments to reduce underfilm corrosion(scribe creep) in painted systems, atmospheric corrosion, pitting corrosion(Al), filiform corrosion(Al) and galvanic corrosion have been developed so far.

Furthermore, before the silanes can be introduced in many industrial environments, more R&D has to be performed. Specifically, what has to be done to develop the treatments into robust industrial processes(i.e. baths must be made more stable, additives developed that reduce the rate of condensation, sensitivity to contaminants and drag-in must be determined and improved, and new silanes developed).

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