

Coatings for Rubber Bonding and Paint Adhesion

M.S. Boulos and M. Petschel

Conversion coatings form an important base for the adhesion of paint to metal substrates and for the bonding of rubber to metal parts. Four types of conversion coatings were assessed as base treatments for the bonding of rubber to steel and for the corrosion protection of metal substrates under paint: amorphous iron phosphate, heavy zinc phosphate, and three types of modified zinc phosphates that utilized one or more metal cations in addition to zinc. When applied, these conversion coatings formed a thin film over the metal substrate that was characterized by scanning electron microscopy, x-ray diffraction, and chemical methods. The performance of the coatings was assessed using physical methods such as dry adhesion, conical mandrel, impact, and stress adhesion for the rubber-bonded parts, and by corrosion resistance methods such as humidity, salt spray, and cyclic corrosion. Coating characterization and performance were correlated.

Keywords conversion coating, iron phosphate, metal pretreatment, surface bonding, zinc phosphate

1. Introduction

The bonding of organic coatings, paints, and rubber to metallic surfaces is an important commercial aspect of metal use and corrosion protection. New alloys have provided remarkably effective solutions to many difficult corrosion problems; however, improved adhesion of organic finishes to metallic parts is an area of ongoing study. Chemical surface conversion treatments remain the most important aspect of metal preparation for achieving effective adhesion of organic finishes to metallic surfaces.

Chemical surface conversion treatments based on phosphate salts are most widely used. Typically, these treatments react with the metallic surface to produce a conversion coating, chemically anchored to the surface, that can provide a corrosion-resistant base to which organic paints and rubber can bond. Phosphate coatings are derived from solutions containing alkali metal phosphate alone (known as iron phosphates), zinc dihydrogen phosphate alone (zinc phosphates), or zinc in combination with other divalent metals such as calcium, nickel, cobalt, and manganese. Newer phosphate-based conversion coating technologies operate at lower temperatures, produce less sludge, and deposit a coating in a shorter time. They also contain lower concentrations of heavy-metal ions in the processing solutions than the older technologies.

This paper documents the comparative performance of four types of phosphating solutions that are commonly used as a base for the bonding of rubber to metallic substrates. The phosphating solutions differ in bath content and optimum operating conditions, while the conversion coatings formed differ in chemical composition, morphology, and physical properties. The influence of crystal size and conversion coating type on paint adhesion and corrosion resistance is also discussed.

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2. Background on Chemical Surface Treatments

A complete chemical conversion process includes the efficient cleaning of the metallic surface, followed by application of the conversion coating. The choice of alkaline or acid cleaner depends on the amount and type of surface soils and scale that require removal. Soils left on the surface result in poor conversion coatings that translate into poor rubber bonding or paint adhesion. Cleaning is followed by the chemical conversion process, which both passivates the surface and provides an enhanced surface area for the bond with rubber. Where there is good metal-to-rubber bonding, the metallic surface is under anaerobic conditions and thus oxidative corrosion is not a concern. Areas that have no rubber bonded to them may require additional corrosion protection through application of a seal or posttreatment after the phosphate conversion coating. With paint films, the low porosity of the organic coating will retard the transport of water and oxygen to the surface and impart some general corrosion resistance. However, the barrier and chemical resistance properties of the conversion coating add significantly to the corrosion-inhibiting characteristics of the total system.

Surface conversion treatments based on phosphating solutions are essentially electrochemical processes in which the oxidation of the metal occurs at the microanodes and the deposition (hydrolysis) of insoluble phosphates occurs at the microcathodes. The conversion coatings formed differ in chemical composition, morphology, and physical properties, yet they have the dual function of enhancing the adhesion of rubber or paint to the metallic substrate and of providing a protective barrier to metallic corrosion.

The standard conversion coatings used in the rubber bonding industry are the heavy zinc phosphates and the calcium-modified zinc phosphates. This paper compares these two industry standards with the newer technology of polycrystalline phosphates that impart a fine crystalline morphology to the metallic surface, and with non-heavy-metal phosphates that provide an amorphous base with enhanced surface area for bonding. Superior performance is demonstrated using these newer technologies.

2.1 *Heavy Zinc Phosphates (Ref 1)*

These phosphating baths form a heavy crystalline conversion coating of 22 to 65 g/m^2 (2000 to 6000 mg/ft^2). The coating consists of a mixture of hopeite [$(Zn_3(PO_4)_2 \cdot 4H_2O$] and phosphophyllite [$(Zn_2Fe(PO_4)_2 \cdot 4H_2O$]. These types of phosphating solutions are regarded as "old technology" since they typically operate at high temperatures of 77 to 88 °C (170 to 190 °F), require long processing times, produce large amounts of sludge, and operate using large amounts of zinc. The crystals are large and overlapping (Fig. 1).

2.2 *Calcium-Modified Zinc Phosphates (Ref 1)*

These phosphating baths form crystalline conversion coatings that are a mixture of hopeite and rhombic scholzite crystals [$Zn_2Ca(PO_4)_2 \cdot 2H_2O$]; the proportion of calcium in the coating is directly related to the calcium in the phosphating bath. Calcium imparts a fining action to the bath (Fig. 2). Coating weights are typically in the 4 to 9 g/m^2 (400 to 800 mg/ft^2) range. The process requires high temperatures of 70 to 82 °C (160 to 180 °F) and produces large amounts of sludge.

2.3 *Polycrystalline Zinc Phosphates (Ref 2)*

This technology incorporates nickel and manganese into the phosphate crystal to form the pseudophosphophyllite structure shown in Fig. 3(a). The advantage derived from this incorporation is most apparent on zinc surfaces, where both wet and dry paint adhesion is improved. The coatings are applied at temperatures between 40 and 52 °C (105 and 125 °F), and coating weights range from 2 to 3 g/m^2 (175 to 250 mg/ft^2) on cold-rolled steel and from 2 to 4 g/m^2 (200 to 350 mg/ft^2) on zinc surfaces. Figure 3(b) shows the percentage of metals incorporated into the conversion coating in an immersion application of a polycrystalline phosphate.

2.4 *Non-Heavy-Metal Phosphates (Ref 3)*

These phosphating baths form amorphous coatings of low weights in the range of 0.3 to 1.0 g/m^2 (25 to 100 mg/ft^2) (Fig. 4). The coating consists of a mixture of vivianite and magnetite, which together provide a topography with enhanced ability for bonding to organic coatings. The phosphating solutions are free of heavy metals and typically operate at low temperatures in the 43 to 60 °C (110 to 140 °F) range.

3. Results and Discussion

3.1 *Treatments for Rubber Bonding*

As stated in section 2, the standard conversion coatings used by the rubber bonding industry are the heavy zinc and calcium-modified zinc phosphates. In this work, these two industry standards were outperformed by the newer technology of polycrystalline phosphates, which impart a fine crystal morphology, and by the new generation of non-heavy-metal phosphates, which provide an amorphous base with enhanced surface area for bonding.

The rubber bonding studies were conducted on postvulcanized rubber systems where curing adhesives are used to create the rubber-to-metal bond. Constant advances are being made in both the chemical nature of adhesives and their application technology. Water-based adhesives are gaining in popularity due to their favorable environmental impact when compared with solvent-based types. Solvent-based adhesives are generally perceived as performing better than water-based adhesives. This is often partly due to the ability of solvent-based adhesives to solubilize residual soils on the metal surface. Water-based adhesives do not contribute to surface cleaning.

The performance of the four types of phosphate conversion coatings outlined in section 2 was compared using two phenolic-type solvent-based adhesives from two different manufacturers and one type of water-based adhesive. Steel parts were cleaned, then treated with the corresponding phosphate conversion coating to which the adhesive was applied. Uncured rubber was superimposed on the adhesive, and bonding was effected during the curing process.

The adhesion properties of these pretreatments under a solvent-based adhesive and natural rubber combinations were characterized using percent adhesion at 9 kN/m (50 lib/in.) of pull before and after salt spray exposure according to ASTM B 117. The results in Fig. 5 show that the percent adhesion at 9

Fig. 1 Heavy zinc phosphate conversion coating crystal morphology

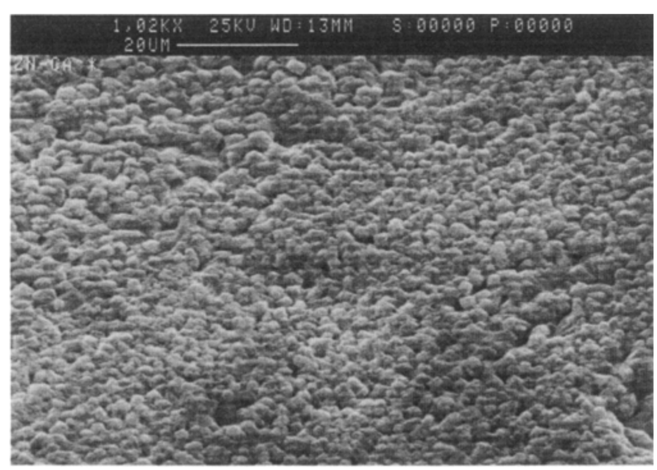


Fig. 2 Calcium-modified zinc phosphate conversion coating crystal morphology

kN/m (50 lb/in.) of pull is essentially equivalent for all the systems except the heavy zinc treatment. The values shown in Fig. 6 after 72 h of salt spray exposure reflect the same observation. (The fact that the value for the heavy zinc coating has increased while the other values have essentially remained the same is not explained at this time.) Failure of the heavy zinc treatments occurred at the adhesive-to-metal interface, suggesting that the thick phosphate layer formed was friable and lacked the cohesive integrity to sustain adhesive strength.

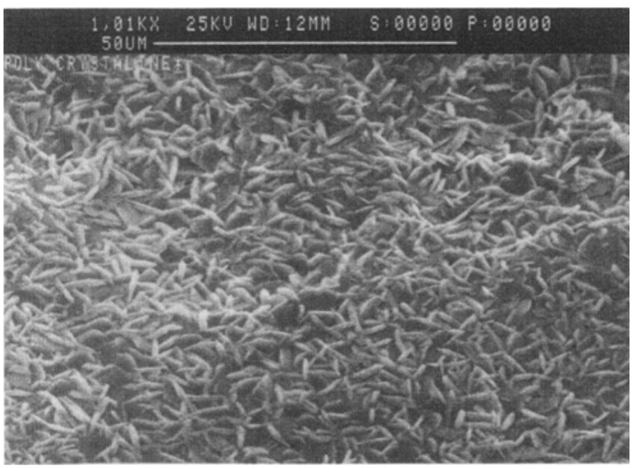
The rubber bonding properties of these conversion coatings under a water-based adhesive and natural rubber combination are shown in Fig. 7 and 8, which give the percent adhesion at 9 kN/m (50 lb/in.) of pull before and after 72 h of salt spray, respectively. Again, the heavy zinc conversion coating yielded the poorest performance under this rubber bonding combination, and again the failure occurred at the adhesive-to-metal interface, suggesting low adhesion to the large crystals associated with the heavy zinc conversion coating.

Further testing was conducted using a solvent-based adhesive from a second adhesive manufacturer and bonded panels. The panels were treated with five conversion coatings and assessed in humidity testing according to ASTM D 2247. Figure 9 shows that the highest rating was obtained with the polycrystalline coating. The amorphous conversion coatings were next best, and the heavy zinc phosphate showed the poorest performance.

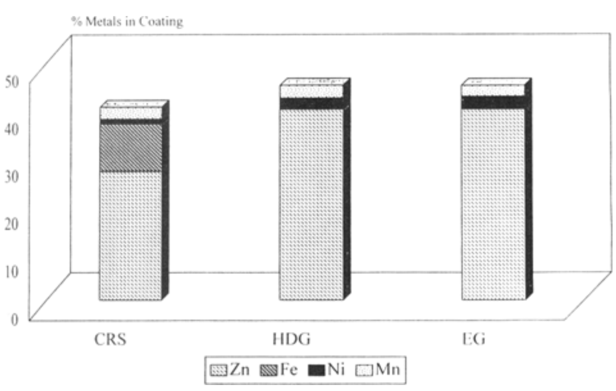
Similar results were obtained in an adhesion test (Fig. 10). Here the maximum pull was again achieved with the polycrystalline and the amorphous conversion coatings. The lowest values were observed for the heavy zinc phosphate conversion coating.

The humidity test results in Fig. 9 also compare amorphous conversion phosphate coatings that differ in the type of posttreatment applied. Results indicate that posttreatment was not a significant contributor to the humidity response. Usually, the corrosion barrier created by these amorphous phosphate systems does not measure up to the corrosion barrier of polycrystalline phosphates, as measured by this humidity test.

An indication of the importance of the type of testing conducted is seen in Fig. 10, where the results of the characteristic of average pounds of pull-to-failure are shown for the same systems discussed in Fig. 9. Here the amorphous coatings show



(a)



(b)

Fig. 3 Polycrystalline zinc phosphate conversion coating. (a) Crystal morphology. (b) Composition (derived from an immersion system). CRS, cold rolled steel; HDG, hot dipped galvanized; EG, electro galvanized

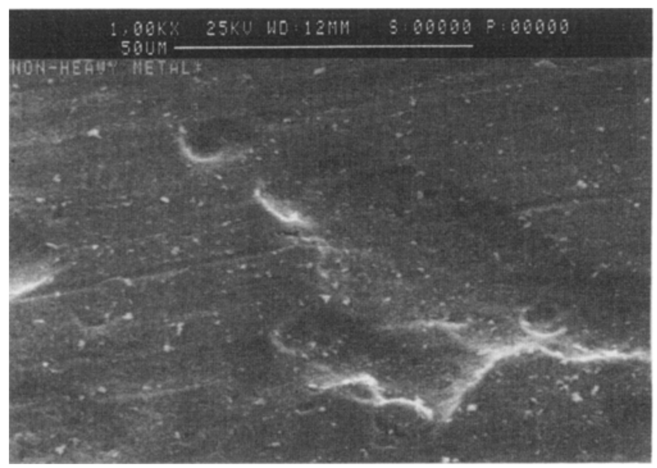


Fig. 4 Non-heavy-metal phosphate conversion coating amorphous morphology

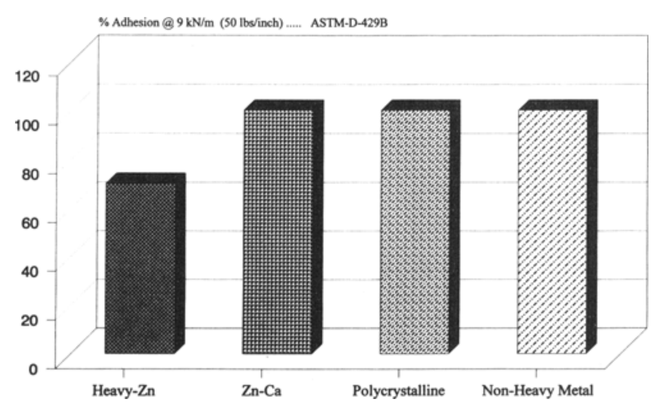


Fig. 5 ASTM D 429B adhesion performance of four phosphate conversion coatings under solvent-based adhesive/natural rubber

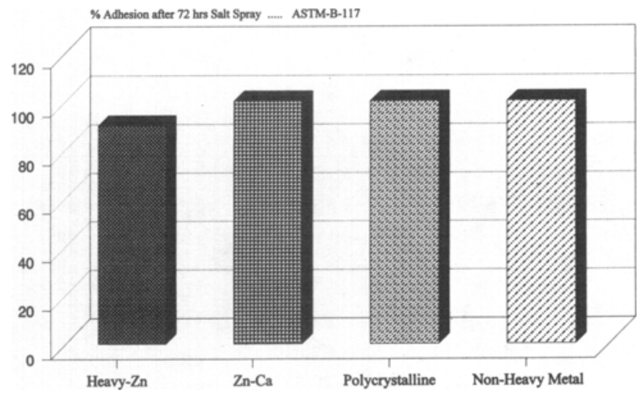


Fig. 6 ASTM B 117 salt spray performance of four phosphate conversion coatings under solvent-based adhesive/natural rubber

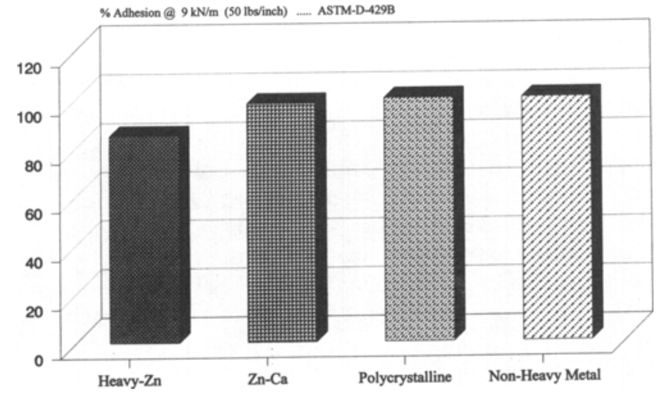


Fig. 7 ASTM D 429B adhesion performance of four phosphate conversion coatings under water-based adhesive/natural rubber

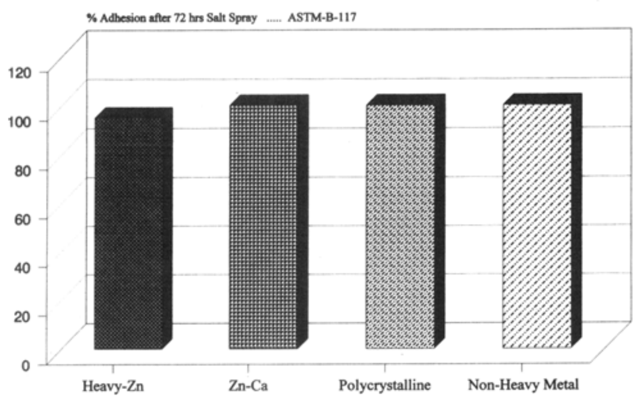


Fig. 8 ASTM B 117 salt spray performance of four phosphate conversion coatings under water-based adhesive/natural rubber

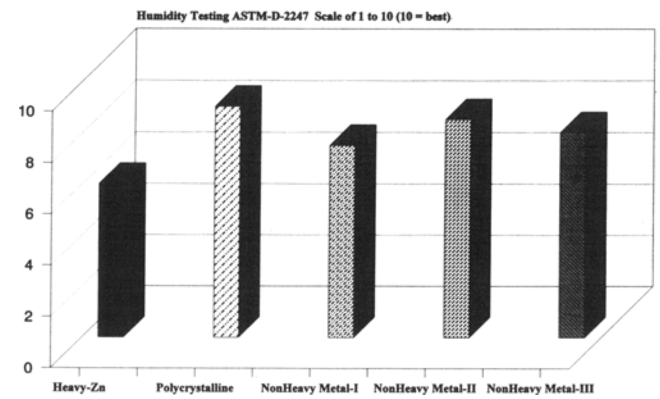


Fig. 9 ASTM D 2247 humidity testing of five phosphate conversion coatings under solvent-based adhesive/natural rubber. Non-heavy metal I: no posttreatment. Non-heavy metal II: organic posttreatment and dried on. Non-heavy metal III: organic posttreatment and rinsed with deionized water. Scale of 1 to 10 (10 = best)

Table 1 Crosshatch adhesion performance under two paint systems(a)

Coating method	Coating weight, g/m^2	Standard paint	High-solids paint
Polycrystalline phosphate	2.2	10	10
Non-heavy-metal phosphate	0.65	10	10
Cleaned-only steel panel	0	6	7

(a) Rating is on a scale of 1 to 10, where 10 = best performance.

a higher value to failure than the polycrystalline coating. This proves that the amorphous coatings present the maximum interfacial characteristics for adhesion in rubber bonding applications. The same is true for paint film adhesion, as will be shown in the next section. The intentional formation of small crystals in zinc phosphates is based on these observations made with non-heavy-metal systems.

3.2 *Treatments for Paint Adhesion*

Crystal size and coating weight have long been topics of discussion and study for painted steel surfaces. Phosphate conversion coatings that impart coarse crystals or high coating weights (e.g., heavy zinc or calcium-modified zinc phosphates) typically are not used. In practice, use of an advanced paint system may hide the contribution of the conversion coating to adhesion. Therefore, choices of paint quality and of the accelerated test to conduct are important criteria in the evaluation of different aspects of adhesion.

A polycrystalline zinc phosphate was compared with a non-heavy-metal (amorphous) phosphate when applied to steel and painted with drum stock paints differing in their solids content and final film characteristics. Coating weights were 2.2 g/m^2 (200 mg/ft^2) for the polycrystalline coating and 0.65 g/m^2 (60 mg/ft^2) for the non-heavy-metal coating. The two paints used in the study were a standard paint and a high-solids paint, both applied 1 mil thick and cured according to their specifications. Adhesion differences were expected since the high-solids paint is less flexible than the standard paint. As a control, panels that had been cleaned but not coated were also painted. Adhesion testing was conducted using two methods: (1) ASTM D 3359 crosshatch adhesion and (2) reverse impact conducted at impact levels of 9, 14, and 18 kg (20, 30, and 40 lb). The results are shown in Tables 1 and 2, respectively.

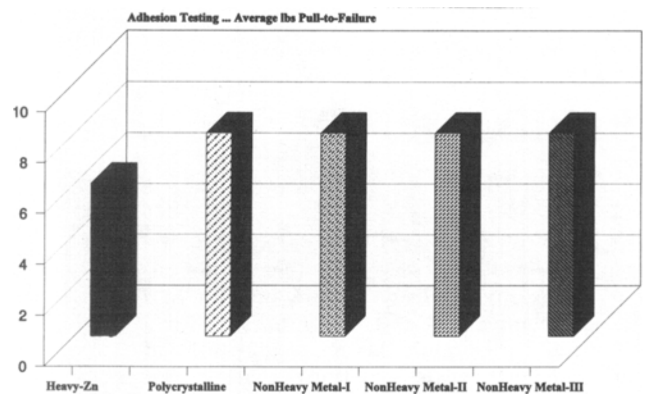


Fig. 10 Relative adhesion testing of five phosphate conversion coatings under solvent-based adhesive/natural rubber. Average pounds for pull-to-failure. See Fig. 9 for description of non-heavy-metal posttreatments.

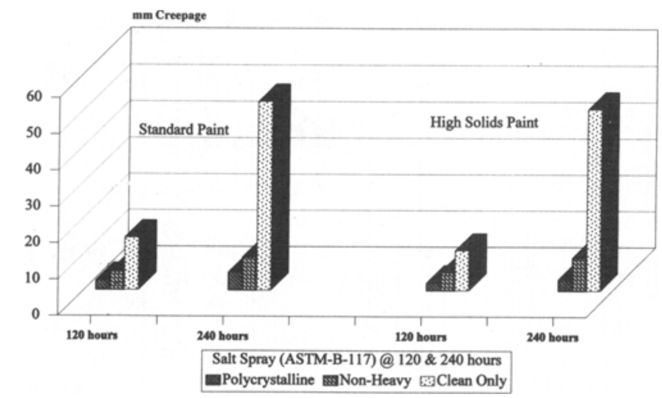


Fig. 11 ASTM B 117 salt spray performance under two paint systems

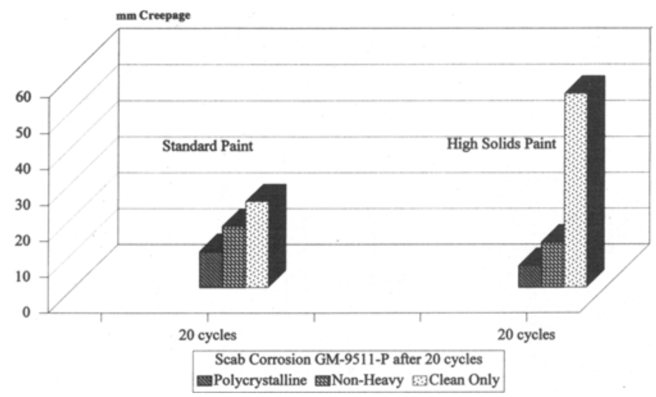


Fig. 12 GM 9511P cyclic corrosion performance under two paint systems

Results of the crosshatch adhesion test (Table 1) show that the two phosphate coating systems had equally good adhesion. This is expected since this test demands no contribution from the crystal structure or size.

Unlike the crosshatch test, the reverse impact test (Table 2) puts a distortion on the conversion coating crystals and crushes them. In this test the amorphous coating fared much better at the higher impact levels than the crystalline coating with both the high-solids and the standard paint. The performance of the cleaned-only panels with the standard paint is surprisingly good, but probably reflects excellent adhesion of this paint to bare metal.

Testing results for salt spray and cyclic corrosion are shown in Fig. 11 and 12, respectively. As anticipated, the cleaned-only method provides no corrosion protection, while the polycrystalline zinc phosphate outperformed the amorphous phosphate in both tests. This superior corrosion resistance is the overriding characteristic that rules in favor of the polycrystalline conversion coatings, even though amorphous coatings provide excellent adhesion. Both coating weight and composition contribute to this difference.

Table 2 Reverse impact performance under two paint systems

	Impact level(a), kg					
	Standard paint			High-solids paint		
Coating method	9	14	18	9	14	18
Polycrystalline phosphate	2P	2P	2P	N	1P	2P
Non-heavy-metal phosphate	N	N	1P	N	N	N
Cleaned-only steel panel	N	N	1P	2P	2P	3P

(a) P = peel; paint peel on a scale of 1 to 10. N = nil; no paint peel.

4. Conclusions

The same conclusions can be drawn for rubber bonding applications and for organic paint film applications. In all cases, superior adhesion characteristics were demonstrated by the amorphous conversion coatings and by the polycrystalline conversion coatings, which imparted a fine crystalline morphology to the metallic surface that markedly improved adhesion of organic finishes. Conversion coatings that consist of large crystals tend to produce poor results under tensile forces, due to fracture or breakage of the large crystals when subjected to torque and impact forces.

A high coating weight is important as a barrier where corrosion protection is needed. The ideal coating weight appears to lie between 1.4 and 2.7 g/m^2 (130 and 250 mg/ft^2). Coating weights above 2.7 g/m^2 (250 mg/ft^2) exhibit reduced mechanical properties due to fracture under stress. Coating weights below 1.0 g/m^2 (100 mg/ft^2) show reduced salt spray performance because they do not form a large corrosion barrier. Polycrystalline phosphate conversion coatings are the best choice when both adhesion and corrosion protection are required.

References

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