NEW CHROMIUM- FREE PRETREATMENTS FOR COIL COATING[1]

Ron Weldon [2]
Karl A. Korinek[2]

INTRODUCTION

Hexavalent chromium containing pretreatments have a long history of successful use in the coil coating industry. The major uses of chromates have been in the pretreatment of aluminum coils for the architectural, can end stock and other applications. In the steel coil coating segment, chromates have mostly been used as pretreatments for zinc-aluminum alloy coated steel or as final rinses for all substrates.

For many years, the users of hexavalent chromium compounds in the United States have been under increasing pressure from the regulations governing plant discharges (Clean Water Act, Resource Conservation and Recovery Act), the worker exposure (OSHA) and the chemical toxicity (TSCA). The coil coating industry has effectively addressed these issues by introducing effective waste treatment facilities to control plant discharges and plant practices to minimize the worker exposure to the Cr (VI) chemicals.

More recently, the new European Directives on Waste Electrical and Electronic Equipment (WEEE) [1] and The Restriction of Hazardous Substance in Electrical and Electronic Equipment (RoHS) [2] restrict the use of certain hazardous substances in new electrical and electronic equipment, such as household appliances, information technology, telecommunications equipment and lighting. From July 2006, new electronic equipment will not be allowed to contain lead, mercury, cadmium, hexavalent chromium, This directive has a direct relevance to the coil coating lines, because RoHS restricts the use of hexavalent chromium, used in pretreatments, paint primers and of lead pigments used in paints. RoHS is becoming a driving force for hexavalent chromium-free products in these markets.

1 *43rd Rolling Seminar – Processes, Rolled and Coated Products, October 17th to 20th, 2006 – Curitiba – PR – Brazil*
2 *Henkel Technologies, Henkel Corporation*

The original RoHS directive has been amended with the purpose to establish the maximum concentration values for these hazardous substances in electrical and electronic equipment. It sets the maximum concentration of 0.1% by weight in homogeneous materials for lead, mercury, hexavalent chromium, PBB and PBDE and of 0.01% by weight in homogeneous materials for cadmium. "Homogeneous" means a material that cannot be mechanically disjoined into different materials and must have uniform composition throughout.

Another European Directive on End-of-Life Vehicles (ELV) [3] is concerned with cars, vans and certain three-wheeled vehicles. It is aimed at making vehicle dismantling and recycling more environmentally friendly and to increase the use of recycled materials in vehicle manufacturing. The vehicle components, placed on the market after July 2003 should not contain mercury, hexavalent chromium, cadmium or lead, except in certain cases. Hexavalent chromium compounds used in corrosion preventions coatings are exempted until 1st July 2007. The ELV directive will also become a driving force for hexavalent chromium-free pretreatments and primers in automotive applications after July 2007.

The elimination of hexavalent chromium use in metal finishing has been discussed by the industry for more than twenty years. In the post-paint operations, the automotive parts manufacturers and automotive OEM's initiated the elimination of hexavalent chromium rinses in mid-eighties and completed the process in mid-nineties. The appliance manufacturers have also completed the conversion to chromium-free rinses during the same period.

In the coil coating industry, the issue of hexavalent chromium elimination is more complicated. Only a relatively small percentage of components for electronic appliance and automotive industries are coated on the coil lines, which usually run products for many end use customers and applications. Another complicating factor for the coil coating industry has been the use of the strontium chromate pigments in the primer coatings used in coil coating. These primers have established a great performance record in the construction segment and continue to be widely used in these high performance applications. The demand for hexavalent chrome-free coating systems in the architectural market has not yet been strong.

In response to this new niche market opportunity, Henkel has developed and introduced to the coil coating industry novel chromium-free pretreatments and/or final rinses based on Henkel's patented Ti/polymer technology, which can provide comparable performance to the hexavalent chromium based pretreatment processes and meet the RoHS requirements.

EXPERIMENTAL

Panel Preparation.

Commercial low carbon cold rolled steel (CRS) and G-90 hot dipped galvanized (HDG) were used as substrates. Panels were processed using sequences, which simulated the different coil coating processes. For the dry-in-place coatings, the processing included: spray cleaning with alkaline cleaner, spray hot water rinsing, drying and application of the dry-in-place coating on the laboratory coater.

For the conventional conversion coating/final rinse applications and the combined conversion coating/dry-in-place application (duplex coatings), the processing included: spray cleaning with alkaline cleaner, spray hot water rinsing, spray applications of conversion coating, spray cold water rinsing and a final chromate rinse or an application of the dry-in-place coating on the laboratory coater. The pretreated panels were dried in an IR oven.

Coating Analysis.

Coating weight determinations were made by acid stripping followed by analysis of metals by atomic absorption spectroscopy and by weigh-strip-weigh method. The Auger surface analysis data were collected using a Physical Electronics PHI 660 Scanning Auger Microprobe. The depth profiles were performed using a differentially pumped argon ion gun. The sputter rate was determined to be 10.5 nm per minute. All reported depths are relative to the silicon dioxide standard.

Painted Performance Testing.

The pretreated panels were painted using a drawdown bar and cured in air circulating oven according to the paint supplier specification. The evaluations have been done according to the following methods:

Adhesion :
T-bend: ASTM D 4145
Reverse Impact: ASTM D 2794

Accelerated Testing:
Neutral Salt Spray: ASTM B 117 – corrosion evaluation according to ASTM D 1654.
Table 1 shows the rating system used for evaluating corrosion creepage in salt spray testing, according to ASTM method D 1654.

Humidity: ASTM D 2247

THE DEVELOPMENT OF CR-FREE PROCESS

To develop a new process, we have first reviewed and compared the regulatory status of the various metal ions, which were considered to be used in the chrome-free treatments. There are no regulatory limits for titanium, which make the titanium based formulations good candidates for the new processes.

Our optimization studies have started with steel substrates where good adhesion and corrosion protection has always been more difficult to achieve. The evaluation included various cationic and anionic additives to the titanium-based systems with various types and ratios of water-soluble polymers.

The coating performance data of the optimized Cr-free formula are shown in Table 2. The results describing the performance with two white single coat polyesters from Specialty Coatings Company, Inc. show that the chrome-free coating has ratings comparable to the chromate controls in salt spray corrosion tests and adhesion tests. The promising performance of this coating, commercially known as Bonderite® 1455, was also confirmed on other substrates with many paint systems.

The preferred application of Bonderite® 1455 coating is by the reverse roll coating on a roll coater to ensure a uniform film application across the strip. More simple chemical coaters, using direct roll coating, have also been successfully used. Bonderite® 1455 coating can be used as a dry-in-place coating, applied directly to the substrate, or in combination with other conversion coatings, such as iron phosphates, zinc phosphates or complex oxide coatings, in so-called duplex coatings, which have recently been introduced to the industry. A solvent-free version of Bonderite® 1455, designated Bonderite® 1455SF is also available.

The coating chemistry is based on the titanium fluoride complex, manganese salts, water-soluble organic polymer and phosphoric acid. Bonderite® 1455 coating has been characterized by Auger spectroscopy. The depth profile of the titanium/phosphate/polymer coating is shown in Fig.1. The alkaline cleaning of CRS gives a surface, which is primarily iron oxide, approximately 10 nm thick, with carbon, phosphorus and calcium contaminants, which are only detected at the surface. In the coating, carbon, titanium, oxygen, iron is the major detected elements, with small amounts of phosphorus also present. These elements are uniformly distributed throughout the coating. The total coating thickness was estimated to be about 150 nm for a 13 mg/sq.ft. of Bonderite® 1455 coating. All components correlate well with each other.

THE DEVELOPMENT OF RoHS COMPLIANT COATINGS

The RoHS compliant coatings require not only a hexavalent chromium free pretreatment but also a non-chromium primer. In order to evaluate the performance of the duplex Bonderite® 902/Bonderite® 1455SF coatings on CRS, we carried out initial panel evaluations with new urethane non-chromium primer and compared it to chromium containing primer. The salt spray results for the two primers for Bonderite® 902 /Bonderite® 1455SF system and Bonderite® 902/Parcolene® 62 chromate rinse controls are shown in Table 3. The manufacturer’s refrigerator specifications require the maximum under film corrosion to be less than 6.4 mm after 500 hrs of salt spray. The salt spray corrosion results on CRS after 504 hrs for the RoHS compliant system were as good as, or better than the chromate controls.

While there are some differences in the comparative performance of the different systems, the results show that the RoHS compliant system shows comparable corrosion results to the chromium containing controls and meets the manufacturer's specifications. The panel studies were extended to HDG, and the results for the duplex Bonderite® 1421/Bonderite® 1455SF and Bonderite® 1303/Bonderite® 1455SF coatings are shown in Tables 4 and 5. For HDG, we extended the salt spray testing to 1008 hrs. On HDG, the RoHS compliant system appeared to be slightly weaker than the chromium based system, but well within the manufacturer requirements. The results of physical testing and humidity testing were also comparable to the controls and well within the manufacturer's requirement specification.

Based on these promising panel results, CRS and HDG production coils were processed with the new RoHS compliant coatings on a coil coating line. The physical properties of the coatings, humidity resistance, stain resistance and salt spray from the trial coils were evaluated. The results were compared to the chromate containing controls. While minor differences in results were observed, the changes were well within specifications. Table 6 shows the results of salt spray corrosion testing of the trial of Valspar's paint systems. On CRS, the salt spray corrosion results of chromium and non-chromium systems were very similar. On HDG, the results with non-chromium primer were slightly weaker, but with a maximum creep of 1.5 mm, well within the manufacturer's specification. The RoHS compliant systems for pre-painted appliance applications are now in full production.

CONCLUSION

A new titanium/phosphate/polymer coating for has been developed as a possible replacement for the chromate based coatings for the coil coating dry-in-place applications. When combined in the " duplex" coatings with the traditional conversion coating systems, such as iron phosphates on CRS, or zinc phosphates or complex oxide coatings on HDG, the new coating systems have been shown to meet the requirements of the RoHS for pre-painted appliance applications, with selected Cr-free primers. With the increased emphasis on hexavalent chromium free systems in new electrical and electronic equipment, such as household appliances, these coatings are finding many commercial applications.

REFERENCES:

1. Directives 2002/96/EC and 2003/108/EC of the European Parliament and Council
2. Directive 2002/95/EC of the European Parliament and Council
3. Directive 2000/53/EC of the European Parliament and Council

TABLE 1

EVALUATING CORROSION CREEPAGE IN SALT SPRAY

ASTM Method D 1654

(Read from scribe to unaffected paint)

ASTM	MEAN CREEPAGE (mm)	ASTM	MEAN CREEPAGE (mm)
10	0.0	5	3.0-5.0
9	0.0-0.5	4	5.0-7.0
8	0.5-1.0	3	7.0-10.0
7	1.0-2.0	2	10.0-13.0
6	2.0-3.0	1	13.0-16.0
		0	16.0 +

TABLE 2

PAINT PERFORMANCE COMPARISON
CRS

	POLYESTER (408-1-W-249)		POLYESTER (408-1-W-247)	
	POLYMER BASED COATING	**CHROMATE CONTROL**	**POLYMER BASED COATING**	**CHROMATE CONTROL**
SALT SPRAY (ASTM RATINGS)				
168 HRS	7	7	6	7
ADHESION				
O-T BEND	10	10	10	10
REVERSE IMPACT	10	10	10	10
COATING WEIGHT				
(MG/FT^2)	12	18	12	18

Specialty Coatings Company, Inc. Coatings:
408-1-W-249 polyester
408-1-W-247 polyester

TABLE 3

PAINT PERFORMANCE COMPARISON
ROHS COMPLIANT COATING ON CRS
SALT SPRAY – 504 HRS

	CHROMIUM PRIMER			NON-CHROMIUM PRIMER		
	MAXIMUM CREEP (mm)	**AVERAGE CREEP (mm)**	**ASTM**	**MAXIMUM CREEP (mm)**	**AVERAGE CREEP (mm)**	**ASTM**
CRS						
Bonderite® 902/Paroclene® 62	6.3	3.1	6	2	1	7.6
Bonderite® 902/Bonderite® 1455SF	4.2	2.4	6	5.9	2.6	6

Valspar's Coatings:
3465 B Epoxy chromium primer, PMW 3855 urethane topcoat.
PTW 9004 urethane non-chromium primer, PMW 3855 urethane topcoat.

TABLE 4

PAINT PERFORMANCE COMPARISON
ROHS COMPLIANT COATING ON HDG
SALT SPRAY – 1008 HRS

	CHROMIUM PRIMER			NON-CHROMIUM PRIMER		
	MAXIMUM CREEP (mm)	AVERAGE CREEP (mm)	ASTM	MAXIMUM CREEP (mm)	AVERAGE CREEP (mm)	ASTM
85101-941 POLYESTER TOPCOAT						
Bonderite® 1421/Parcolene® 62	0	0	10	3.7	0.43	8.7
Bonderite® 1421/Bonderite® 1455SF	0	0	10	6.9	0.7	7.8
PMW 3628 POLYESTER TOPCOAT						
Bonderite® 1421/Parcolene® 62	0.5	0.03	9.7	6.4	1.4	6.7
Bonderite® 1421/Bonderite® 1455SF	5.6	1.0	7.0	3.5	0.25	9.0

Valspar's Coatings:
3465 B epoxy chromium primer
PTW 904 urethane non-chrome primer
85101-941 polyester topcoat
PMW 3628 polyester topcoat

TABLE 5

PAINT PERFORMANCE COMPARISON
ROHS COMPLIANT COATING ON HDG
SALT SPRAY – 1008 HRS

	CHROMIUM PRIMER			NON-CHROMIUM PRIMER		
	MAXIMUM CREEP (mm)	AVERAGE CREEP (mm)	ASTM	MAXIMUM CREEP (mm)	AVERAGE CREEP (mm)	ASTM
85101-941 POLYESTER TOPCOAT						
Bonderite® 1303/Parcolene® 62	5.1	0.6	8.0	5.2	0.4	8.7
Bonderite® 1303/Bonderite® 1455SF	1.5	0.4	8.7	6.4	1.0	7.7
PMW 3628 POLYESTER TOPCOAT						
Bonderite® 1303/Parcolene® 62	0.6	0.1	9.0	6.2	1.1	7.3
Bonderite® 1303/Bonderite® 1455SF	0.6	0.03	9.7	8.2	0.7	8.3

Valspar's Coatings:
3465 B epoxy chromium primer
PTW 904 urethane non-chrome primer
85101-941 polyester topcoat
PMW 3628 polyester topcoat

TABLE 6

PAINT PERFORMANCE COMPARISON
ROHS COMPLIANT COATING ON CRS AND HDG
SALT SPRAY – 504 HRS
LINE TRIALS

	CHROMIUM PRIMER			NON-CHROMIUM PRIMER		
	MAXIMUM CREEP (mm)	**AVERAGE CREEP (mm)**	**ASTM**	**MAXIMUM CREEP (mm)**	**AVERAGE CREEP (mm)**	**ASTM**
CRS						
Bonderite® 902/Parcolene® 62	3.6	1.9	7			
Bonderite® 902/Bonderite® 1455SF				3.0	1.5	7
HDG						
Bonderite® 1303/Parcolene® 62	0	0	10			
Bonderite® 1303/Bonderite® 1455SF				1.5	0.9	8

Valspar's Coatings:
3465 B epoxy chromium primer, PMW 3855 urethane topcoat.
PTW 9004 urethane non-chromium primer, PMW 3855 urethane topcoat.

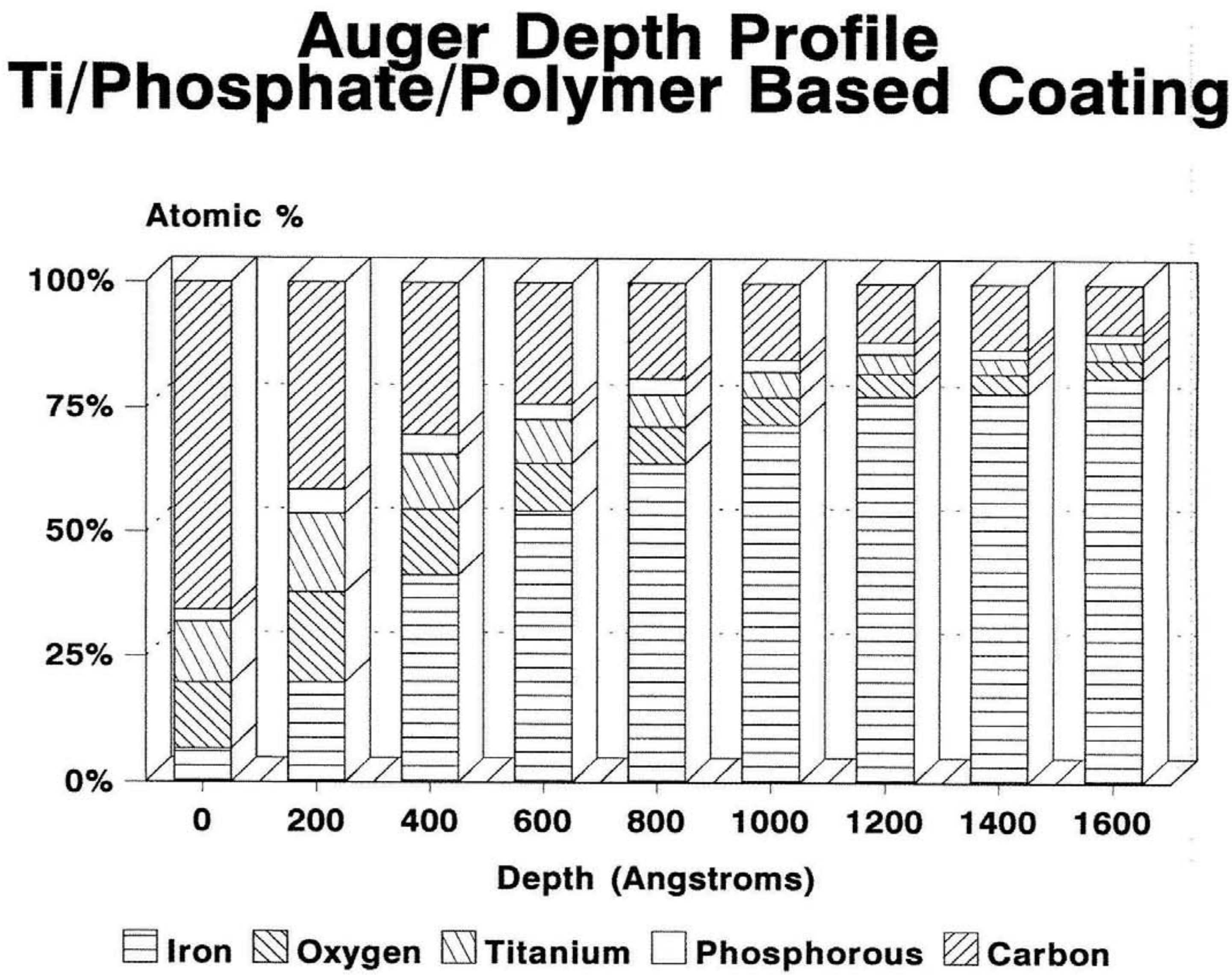

Fig 1: Auger depth profile of Titanium/Phosphate/Polymer based coating on CRS