Technical Article

Non-Polluting Metal Surface Finishing Pretreatment & Pretreatment/Conversion Coating

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Technical Editor's Note: *Since the inception of this journal, it has been our policy that technical papers published in* Plating & Surface Finishing *avoid the use of proprietary or "trade" names. If a distinction between a generic name and a proprietary one is necessary, the latter is usually expressed as a footnote to the text. In this paper however, a proprietary name is germane to the whole presentation. The substitution of a term, such as "proprietary bath formulation," or even its acronym "PBF," severely distracts from a clear reading of this material. In that spirit, a very rare exception to our policy has been made for this paper. This does not however, alter the policy for future papers in this journal.*

Picklex®[**], a proprietary formulation, is an alternative to conventional metal surface pretreatments and is claimed not to produce waste or lower production or performance. A laboratory program was designed to evaluate and compare the process in common, large-scale, polluting surface finishing operations with conventional processes, using steel and aluminum panels, measuring product coating properties, process operability and costs. Twenty-one surface finishing combinations were tested under both "contaminated" and "non-contaminated" conditions with respect to finish adhesion, bending, impact, hardness and corrosion resistance. Results indicated that Picklex® pretreated panels performed as well as panels that were conventionally pretreated, and with a simpler process. It was particularly acceptable for powder-coated steel or aluminum, but may not be applicable to certain metal plates. The results are interpreted in terms of the surface film produced by Picklex®. A use rate of 133 m^2/L (5,400 ft^2/gal) was estimated. Picklex® did not generate by-product waste solids, was effective at room temperature, used short processing times and was easy to use. A field study in an actual powder coating shop was conducted to validate the lab results. An engineering assessment indicated that there are cost advantages as well. This paper focuses on the field study.

Nuts & Bolts: What This Paper Means to You

Picklex®, a proprietary formulation, is an alternative to conventional metal surface pretreatments and is claimed not to produce waste or lower production or performance. This study evaluated and compared it in commercial surface finishing operations with conventional processes, using steel and aluminum panels, measuring coating properties, process operability and costs. Picklex® pretreated panels performed as well as those that were conventionally pretreated. It was particularly acceptable for powder coated steel or aluminum, but may not be applicable to certain metal plates. It generated no by-product waste solids, was effective at room temperature, used short processing times and was easy to use.

Objectives

The overall objective of this study was to evaluate the ability of Picklex® as a metal pretreatment or pretreatment/conversion coat in finishing operations, which can be used to eliminate or reduce the amount of hazardous and toxic chemicals while maintaining equal or better product perfor-

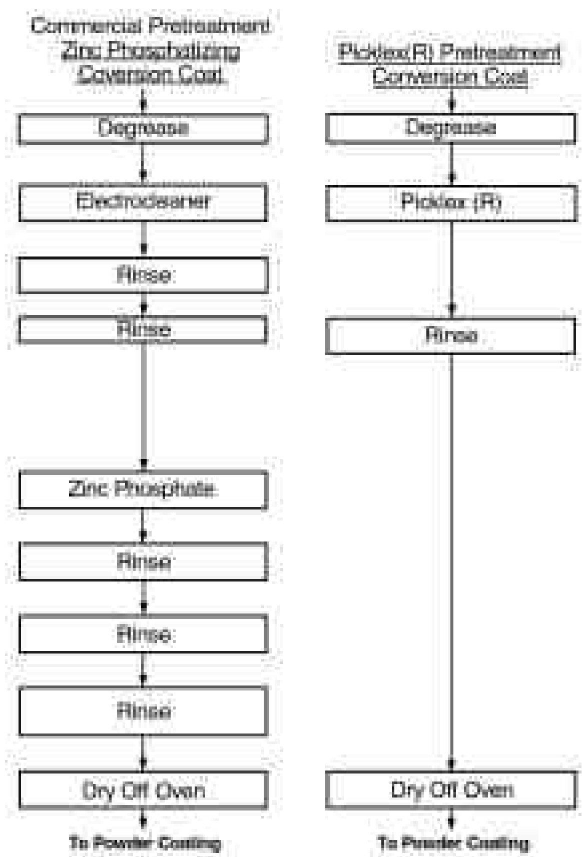

Fig. 1—Processes for commercial zinc phosphate and Picklex® conversion coatings on steel.

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mance properties, with economic benefit for some processes and no significant economic penalty for other processes. Waste reduction would be accomplished through the elimination of processing steps, and hence, the waste stream volumes from these steps, especially those processes involving ventilation of warm or gassing solutions. These improvements are expected to decrease production costs. The cost of Picklex® raw material would somewhat offset these savings. The Phase II objective was to evaluate applications for powder coating finishes on aluminum and steel through representative commercial field tests. The evaluation focused on technical performance and economics while validating the previous laboratory tests and environmental benefits.[1]

Table 1
Test Matrix for Both Contaminated & Noncontaminated Panels

Index	Test System ID(a)	Basis Metal	Pretreatment System	Conversion Coating	Final Finish
1	Fe-C-ZnP-PC			Zinc Phosphate	Powder Coat
2	Fe-C-N-HCr			None	Hard Chromium
3	Fe-C-N-ENi	Low-carbon steel (C1010)	Conventional	None	Electroless Nickel
4	Fe-C-N-Zn			None	Electrolytic Zinc
5	Fe-C- NiS-N			Nickel Strike	None
6	Fe-C-P-PC			Picklex®	Powder Coat
7	Fe-P-ZnP-PC			Zinc Phosphate	Powder Coat
8	Fe-P-N-HCr			None	Hard Chromium
9	Fe-P-N-ENi	Low-carbon steel (C1010)	Picklex®	None	Electroless Nickel
10	Fe-P-N-Zn			None	Electrolytic Zinc
11	Fe-P- NiS-N			Nickel Strike	None
12	Fe-P-PC(b)			Picklex®	Powder Coat
13	Al-C-N-N			None	None
14	Al-C-N-PC			None	Powder Coat
15	Al-C-Cr-N	Aluminum Al 2024 or Al 3105	Conventional	Chromate	None
16	Al-C-Cr-PC			Chromate	Powder Coat
17	Al-C-P-PC			Picklex®	Powder Coat
18	Al-P-N-N			None	None
19	Al-P-Cr-N	Aluminum Al 2024 or Al 3105	Picklex®	Chromate	None
20	Al-P-Cr-PC			Chromate	Powder Coat
21	Al-P-PC(b)			Picklex®	Powder Coat

(a) Test system identification (excluding redundant Indexes 12 and 21) consists of four abbreviations separated by hyphens.
First abbreviation is basis metal: Fe = carbon steel, Al = aluminum.
Second abbreviation is pretreatment system: C = conventional, P = Picklex® pretreatment.
Third abbreviation is conversion coating: Cr = chromate, ZnP = zinc phosphate, N = none, P = Picklex®.
Fourth abbreviation is final finish coating: N = none, PC = powder coat, HCr = hard chromium, ENi = electroless nickel, Zn = electrolytic zinc, NiS = nickel strike.
(b) In these tests, Picklex® served as the pretreatment and the conversion coating applied in one step.

Background

Metal surface finishing is a major manufacturing industry consisting of thousands of production shops that provide weather- and wear-resistant and/or aesthetically pleasing manufactured products. The volume of hazardous/toxic waste streams produced from metal surface finishing operations is significant.[2]

It is common for product surfaces to undergo more than ten finishing steps that include degreasing and cleaning (for oil removal and de-scaling), etching, desmutting, pickling, plating and rinsing. The elimination of any of the surface processing steps is desired by manufacturers to reduce processing costs, waste production and energy consumption. With this objective in mind, a no-waste surface-finishing agent designed to provide a nearly one-step metal surface preparation operation for metal finishing operations would be of great benefit. In this study, Picklex® provided metal surface cleaning, pickling, conversion coating and priming using a process simply consisting of degreasing, one dip-step (can also be sprayed), one rinse and then final processing.

Two other partners were involved in this project, particularly in the field testing phase. They were Mills Metal Finishing (Columbus, OH) and an anonymous manufacturing company, identified as Commercial Partner No. 1 in this report.

Pertinent Surface Finishing Processes Tested

Pretreatment processes prepare the surface of the basis metal for conversion coating and final finish (e.g., painting or metal plating). Pretreatment is a critical part of the surface-finishing process because it determines whether the subsequent layers will adhere, and the density of defects. Conversion coatings are performed immediately after the pretreatment operation to preserve the clean surface and to provide the transition "primer" layer between the basis metal and any top coats. Topcoats represent the final finish. The following were selected as representing unique surface finishing features: hard chromium, electroless nickel, zinc plate and powder coating.

Selection of Surface Finishing Test Systems

Twenty-one (21) surface-finishing test combinations were selected for the systematic side-by-side comparisons with Picklex®. These systems were composed of the fundamental surface-finishing operations, each consisting of a series of individual process steps (Table 1). To obtain the Picklex® (P) test system combination, the conventional process step(s) was simply removed and replaced with a Picklex® dip and rinse. Full details of the specific test conditions and process flow schemes used in the bench scale testing are available.[3]

Phase I: Results & discussion

A general description of these test results is provided in Table 2. Specifics are available elsewhere.[3] Coating performance test results include adhesion, bending, burnishing, hardness, impact and salt spray exposure. Table 2 summarizes the comparative test results between Picklex® and the conventional processes. All of the tape adhesion tests for coated aluminum and steel passed at the highest level (5B), namely no paint removal from cross-hatched surfaces. Picklex® offers an advantage over the conventional processes with respect to top coat adhesion because it provided equivalent mechanical strength with fewer and simpler steps as well as reducing waste production.

In the bend tests, no peeling or flaking was observed for all test systems. Therefore, Picklex® passed the pretreatment screening test for powder top coats for 1010 low carbon steel with respect to the bend test.

Table 2
Comparison of Coating Performance Results Of Conventionally Produced Panels versus Picklex®-produced Panels

Coating	Tape Adhesion	Bend	Burnishing	Impact Adhesion	Hardness	Corrosion Resistance
Powder topcoat on aluminum	Equivalent (a), good on contaminated and noncontaminated surfaces	Equivalent (a), passed; no peeling/flaking	NA (b)	Equivalent (a)	NA (b)	Equivalent (a)
Powder topcoat on steel	Equivalent (a), good on contaminated and noncontaminated surfaces	Equivalent (a), passed; no peeling/flaking (c)	NA (b)	Conventional slightly better than Picklex®	NA (b)	Equivalent (a)
Hard chromium	Equivalent (a), good on contaminated and noncontaminated surfaces	Equivalent (a), passed; no peeling/flaking	Equivalent (a), passed	Equivalent (a)	Equivalent (a), good on contaminated and noncontaminated	Conventional slightly better
Electrolytic zinc on steel	Contaminated, conventional failed	Equivalent (a), passed; no peeling/flaking	Picklex® failed lifting, passed blisters and peeling	Picklex® much better on contaminated, equivalent on noncontaminated	NA (b)	Equivalent (a), marginal
Electroless nickel on steel	Contaminated, Picklex® failed	Equivalent (a), passed; no peeling/flaking	Both passed blisters and peeling; only contaminated, conventional passed lifting	Equivalent (a), good	Equivalent (a), good	Equivalent (a), marginal
Conversion-coated aluminum (d)	NA (b)	NA (b)	NA (b)	NA (b)	NA (b)	Equivalent (a), both need chromate for excellent performance

(a) Conventional and Picklex®-pretreated panels provided the same coating performance.
(a) NA = Not applicable.
(b) Cracking of powder topcoat with Picklex® and conventional
(d) Alodine®, Henkel Surface Technologies, Inc., Madison Heights, MI.

Bend test results for hard chromium, electrolytic zinc and electroless nickel coatings on non-contaminated and contaminated steel substrates exhibited some degree of cracking, but only those coatings that could be lifted off using the standard tape were considered to have failed the test. Hard chromium passed the bend test for all pretreatment conditions. The only pretreatment condition that resulted in a bend test failure for electrolytic zinc was with conventionally-pretreated and contaminated steel substrates. We concluded that the contamination level was beyond what could be handled by the conventional pretreatment process. All the Picklex® pretreated steel panels coated with electrolytic zinc passed this test, both non-contaminated and contaminated. It was a significant advantage that Picklex® was able to handle this contamination without having to alter the process. Interestingly, corroded steel substrates using Picklex® as a pretreatment passed the bend adhesion test for electroless nickel coatings, but the non-corroded panels did not. This result may reflect that Picklex® can use surface corrosion conversion products in forming its pretreatment/conversion coat.[4]

Bath Exhaustion Test Results & Conclusions

Corroded steel panels were used for the Picklex® bath exhaustion tests to provide an accelerated test. A total of 2,035 contaminated panels of 1010 low carbon steel with a surface area of 0.193 m^2/panel (39.4 m^2 total) [0.208 ft^2/panel (424 ft^2 total)] were processed through 2.5 L (0.66 gal) Picklex® (15.7 m^2/L; 642 ft^2/gal) over a one-month period. Powder coating properties were tested at regular intervals. The bath condition was also monitored with respect to pH, acid components and visible spectrophotometry.

Based on the UV/visible results, the Picklex® bath was 78% active (22% depleted) after the equivalent of approximately 15.7 m^2 of contaminated steel surface area per liter of Picklex® (642 ft^2/gal) was processed. The active ingredients in surface-finishing baths were not normally fully consumed since the rate of action would become too slow as the reagents became dilute. Using a linear extrapolation of the consumption of active ingredients to 50% would correspond to approximately 35.7 m^2 of surface processed per liter (1450 ft^2/gal) of bath. Using the measured conversion factor of 3.7[3] to convert from contaminated to non-contaminated panels gives an equivalent of 132.6 m^2/L (5400 ft^2/gal) processed.

Picklex® Waste Disposal Assessment

Fresh, spent, and impurity-spiked spent Picklex® samples were treated[3] using the conventional pH 9 precipitation industrial waste water treatment method to produce samples for a waste disposal assessment. The waste solids were assessed for leachability. The treated water supernatants for discharge were also examined and found as most likely dischargeable. Actual discharge limits from industrial waste treatment plant operations are site-specific and are determined on a case-by-case basis with local, state and federal regulatory agencies. Hence, no exact classification of these potential waste solutions is possible until a specific location is known. All leachates passed with respect to 40 CFR 261.[5] Therefore, Picklex® did not appear to present unusual waste treatment issues. Note that the manufacturer claims that the solution, diluted by rinse waters, can be restored by adding a concentrate to the bath. In a separate study[6] the exhausted Picklex® was easily restored. Therefore, waste treatment may not be frequent or necessary in many processes.

Table 3
Comparison of Coating Performance Results of Conventionally Pretreated Panels Versus Picklex® Pretreated Panels —Phases I & II

Coating	Phase	Tape Adhesion	Bend	Impact Adhesion	Corrosion Resistance
China White Powder Topcoat on Aluminum	Phase I	Equivalent (a)	Equivalent (a) passed, while chromated Picklex® conventional cracked with no peeling/ flaking	Equivalent (a)	Equivalent (a)
	Phase II	Equivalent (a)	Equivalent (a) passed	Chromated Picklex® slightly better; conventional chromate had one failure	Equivalent (a)
China White Powder Topcoat on Steel	Phase I	Equivalent (a)	Equivalent (a) passed, cracking with Picklex® and conventional	Conventional slightly better than Picklex®	Equivalent (a)
	Phase II	Equivalent (a)	Equivalent (a) passed	Equivalent (a)	Equivalent (a)

(a) Conventional and Picklex® pretreated panels provided the same coating performance.
(b) Panels processed in Picklex® for 5 min and rinsed in DI water for 45 sec before receiving conversion coat.

Phase II: Field Testing

A broad laboratory evaluation of Picklex® was studied during Phase I for many processes. Following this work, a focused field test for powder coating applications on aluminum and steel was undertaken.

A total of 41 different combinations of substrate, degreaser, pretreatment, conversion coat and powder coat were tested. Only non-contaminated panels and components, without corrosion products, were used. Grade 3105 Aluminum and 1010 low carbon steel panels were used. Aluminum die cast alloy and malleable iron casting components were also processed.

Three batches of panels and/or components were processed at Mills Metal Finishing. The first batch included steel and aluminum panels and served as a process validation in transition from the laboratory to an industrial setting. The second batch included commercial components and panels. The third batch included both components and panels and focused on using a standard powder coat material*** used by Commercial Partner No. 1 on the aluminum components for production use. The coatings were evaluated by a matrix of tests including adhesion, bend adhesion, impact adhesion, hardness and corrosion resistance.

The field testing replicated the results of the laboratory processes. Field testing showed slightly better results for Picklex® than conventional surface-finishing processes for bend and impact adhesion. In general, Table 3 compares results between the two phases for conventionally pretreated panels versus Picklex® pretreated panels.

During Phase II, the immersion time was reduced from 5 minutes to 30 seconds for aluminum and from 5 minutes to 90 seconds for steel (Table 4). Depending on the corrosion resistance needed for the application, shorter Picklex® immersion times might be acceptable. The corrosion resistance on aluminum was equivalent for all other test parameters.

Surface Finishing Procedures

Three different degreasing conditions were used for the field testing. Certain panels in Batch No. 1 were degreased with toluene at Battelle before processing further to replicate the Phase I labora-

*** *Spraylat PE6639M, Spraylat Corp., Mt. Vernon, NY.*

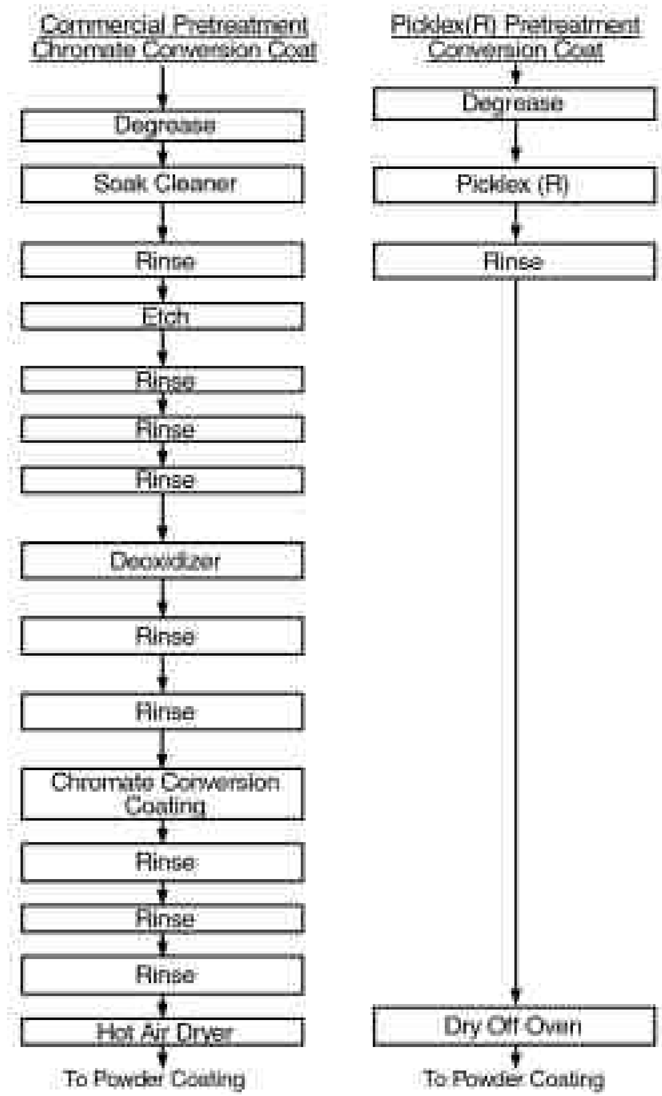

Fig. 2—Processes for commercial chromate and Picklex® conversion coatings on aluminum.

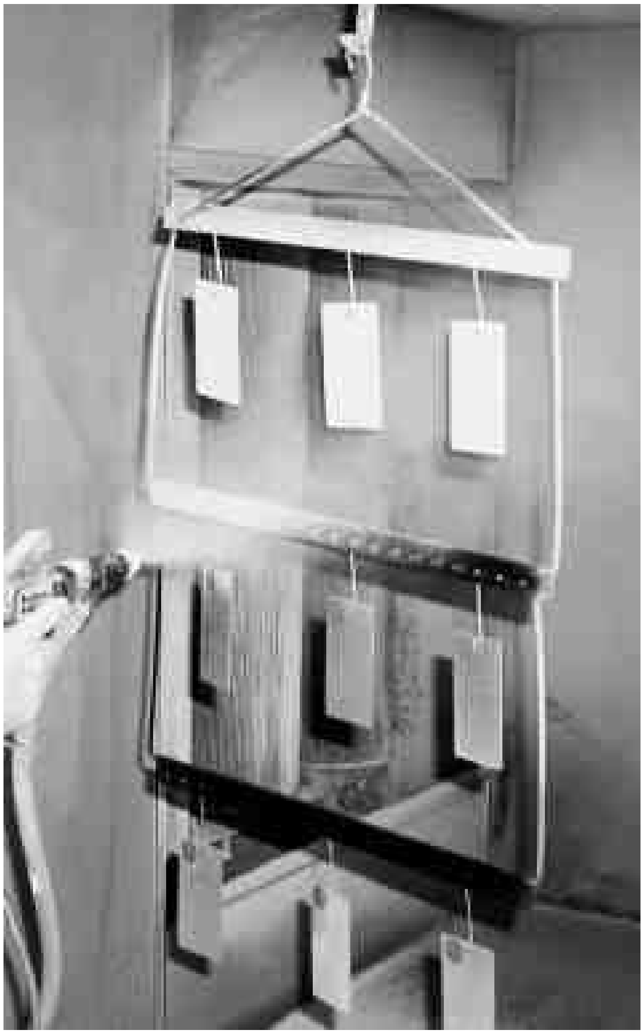

Fig. 3—Powder coating operation.

tory test results. At Mills, certain panels were degreased**** and certain other sets of panels were not degreased

Two pretreatment systems were used for each type of material: commercial pretreatment and Picklex® pretreatment. For aluminum, the pretreatment consisted of Mills' normal process line: soak cleaner, two rinses, etch, two rinses, deoxidizer and two rinses. For steel, each commercial pretreatment consisted of Mills' normal process line, a cleaner and then a series of rinses. For Picklex® pretreatment, Picklex® was used for a specified time and then one rinse was performed at a specified time if at all as per the test sequence. In both cases a conversion coat was followed unless this step was skipped and the Picklex® also served as the conversion coat. The two commercial conversion coatings which were reviewed during field testing were chromate for aluminum and zinc phosphate for steel. Figure 1 illustrates the reduction of process steps with Picklex®.

Technical Performance

This section summarizes the technical performance evaluation by the various coating performance parameters and addresses the economic and overall feasibility issues in engineering assessment.

Test System Designation

Each test system was identified by a combination of nine abbreviations that referenced the substrate material, the degreaser, the pretreatment system, the rinse after pretreatment, the water break test, the conversion coating, the rinse after conversion coating, the dryer and the powder coat material. The abbreviation code used in the report is shown in Table 5.

Table 5
Summary of Results from Materials Testing

					Impact Adhesion			Salt Fog		
Batch	Group	Test ID (a)	Dry Film Thickness Range	Adhesion by Tape Range	Average Impact (foot— pounds)	Sample I.D. of Failures	Sample I.D. of Bend Adhesion Failures	Exposure time (hours)	Adhesion by Tape Range (c)	Creepage Range (d)
ALUMINUM										
1	A	Al-T-C-R-n-Cr-R-A-CW	1.27 - 1.89	5B	40	6		1760	5B	
1	B	Al-T-P5M-R-w-Cr-R-A-CW	1.91 - 2.24	5B	54			1760	5B	
1	C	Al-T-P5M-R-w-N-N-O-CW	1.85 - 2.18	5B	59			1760	4B	
1	D	Al-C-C-R-n-Cr-R-A-CW	1.86 - 2.07	5B	64			1760	5B	
1	E	Al-C-P5M-R-w-Cr-R-A-CW	1.93 - 2.57	5B	65			1760	4B	
1	F	Al-C-P5M-R-w-N-N-O-CW	2.04 - 2.68	5B	66			1760	3-4B	
1	G	Al-T-P5M-R-w-Cr-R-A-SB	1.63 - 2.04	5B	4	13, 10, 3, 18	12	1760	5B	
1	H	Al-C-P5M-R-w-Cr-R-A-SB	1.24 - 1.83	5B	4	11, 2, 8, 18		1760	5B	
1	I	Al-C-P5M-R-w-N-N-O-SB	1.85 - 2.14	5B	4	1, 4, 10, 17		1760	3-4B	
2	Q	Al-C-P30S-R-w-Cr-R-A-CW	1.23 - 2.28	5B	60			1277	5B	

Continueation on next page.

**** *Zep ID Red, Zep Commercial, Inc., Atlanta, GA.*

2	R	Al-C-P30S-N-w-N-N-O-SB	1.42 - 1.77	5B	4	6, 19, 26, 35	3,14,31	1277	3-4B	
2	S	Al-C-P30S-R-w-N-N-O-CW	1.39 - 1.55	5B	46			1277	4B	
2	T	Al-C-P30S-R-w-N-N-O-SB	1.08 - 1.58	5B	4	2, 13, 27, 34	5,23,31	1277	5B	
2	U	Al-C-C-R-w-Cr-R-A-CW	1.14 - 1.30	5B	60			1277	5B	
2	V	Al-C-C-R-w-Cr-R-A-SB	1.29 - 1.99	5B	4	1, 15, 24, 36	5,22,31	1277	5B	
2	X	Al-C-P30S-R-w-Cr-R-A-SB	1.05 - 1.42	5B	5		2,9,22	1277	5B	
2	Y	Al-C-P30S-N-w-N-N-O-CW	1.53 - 2.29	5B	4	8, 17, 25, 29	3,9,32	1277	2-4B	
2	Z	Al-C-P30S-N-w-N-N-O-CW	1.31 - 1.77	4-5B	4	9, 13, 26, 27	3,16,32	1277	0-2B	
2	RR	Al-C-P30S-QR-w-N-N-O-SB	1.03 - 1.38	5B	4	1, 6, 8, 11	3,7,10	1277	2-4B	
2	SS	Al-C-P30S-QR-w-N-N-O-CW	1.35 - 1.82	5B	52			1277	4B	
3	AAA	Al-C-P30S-R-w-Cr-R-A-SA	2.88 - 3.39	2-4B	27		NA (e)	NA		
3	BBB	Al-C-P30S-R-w-N-N-O-SA	2.75 - 2.96	3-4B	35		NA	NA		
3	CCC	Al-C-P30S-QR-w-N-N-O-SA	2.74 - 3.00	4B	37		NA	NA		
					STEEL					
1	J	Fe-T-C-R-w-ZnP-R-O-CW	1.95 - 2.00	5B	20			1760, J2 @1376		7 for J2
1	K	Fe-T-P5M-R-w-ZnP-R-O-CW	1.65 - 2.20	5B	25			1760		
1	L	Fe-T-P5M-R-n-N-N-O-CW	2.13 - 2.35	5B	160			1376		6
1	M	Fe-N-P5M-R-w-N-N-O-CW	2.14 - 2.88	5B	160			1376		5-6
1	N	Fe-C-C-R-w-ZnP-R-O-CW	1.88 - 2.11	5B	7	8.18		1376		6-7
1	O	Fe-C-P5M-R-w-ZnP-R-O-CW	1.68 - 2.82	5B	32			1760		
1	P	Fe-C-P5M-R-n-N-N-O-CW	2.04 - 2.40	5B	18			1376		5-6
2	AA	Fe-C-P90S-R-w-ZnP-R-O-CW	0.93 - 1.34	5B	4	25	21,32,34	893, AA16 @ 608		7-8
2	BB	Fe-C-P90S-R-w-N-N-O-CW	1.22 - 1.74	5B	155			893		5-6
2	CC	Fe-N-P90S-R-w-N-N-O-CW	1.46 - 1.58	5B	158			893		4-5
2	DD	Fe-C-P90S-N-w-N-N-O-CW	1.11 - 1.22	5B	160		22	608		3-4
2	EE	Fe-C-C-R-w-ZnP-R-O-CW	1.22 - 1.69	5B	26		7,16,20	893		6-7
3	GGG	Fe-C-P90S-N-w-N-N-O-CW	2.88 - 3.29	4-5B	30			(b)		

(a) *First abbreviation is basis metal: Al = aluminum panel, Fe = steel panel, AlC = Aluminum component, FeC = steel component.*
Second abbreviation is degreaser: T = toluene, C = Mill's degreaser, N = No degrease step.
Third abbreviation is pretreatment system: C = conventional (Mill's pretreatment), P5M = Picklex® for 5 min, P30S = Picklex® for 30 sec, P90S = Picklex® for 90 sec.
Fourth abbreviation is rinse step after pretreatment system: R = rinse, N = no rinse step after pretreatment.
Fifth abbreviation is water break step: W = water break test, N = no water break test to be performed.
Sixth abbreviation is conversion coating system: Cr = chromate, ZnP = zinc phosphate, N = none.
Seventh abbreviation is rinse after conversion coating system: R = rinse, N = none.
Eighth abbreviation is drying system: O = dry off oven, A = hot air dry off box.
Ninth abbreviation is powder coating system: CW = china white, SA = standard powder coat material for aluminum used during Batch 3, SB = alternate powder coat material for aluminum used during batches 1 and 2, NA = not applicable*
** Spraylat PE6639M, Spraylat Corp., Mt. Vernon, NY.*
*** Spraylat PEB1867C , Spraylat Corp., Mt. Vernon, NY.*
(b) *Sample still in salt fog chamber.*
(c) *Adhesion by Tape test performed after salt fog exposure.*
(d) *Creepage rating performed only on steel panels which had loss of coating adhesion on scribe.*
(e) *NA = not applicable, test not performed*

Tape adhesion

Adhesion by tape was determined by ASTM D 3359. Table 5 lists the adhesion by tape ranges for each group of panels.

Superior results were obtained when comparing adhesion of Commercial Partner No. 1's production parts versus the Picklex® processed parts. Commercial Partner No. 1 provided twelve aluminum components for Batch No. 3 testing to be processed with Picklex®, and finished with their standard powder coat material for aluminum. Upon receipt of the processed components, Commercial Partner No. 1 determined the paint thickness and adhesion by tape using ASTM D 3359. Table 6 shows the tape adhesion results. Tape adhesion was superior for all three variations using Picklex®

Table 4
Effect of Picklex® Process Time

Powder Coating	Process Time	Tape Adhesion	Bend	Impact Adhesion	Corrosion Resistance
China White Powder Topcoat on Aluminum	5 vs. 0.5 min	Equivalent (a)	Equivalent (a)	Equivalent (a) passed with 5-min application receiving slightly higher readings	Equivalent (a)
China White Powder Topcoat on Steel	5 vs. 1.5 min	Equivalent(a)	Equivalent(a)	Equivalent (a) passed with 5-min application receiving slightly higher readings	Depending on application needs, 5-min application had higher corrosion resistance than 90-sec application

(a) Differences in Picklex® processing time provided the same coating performance.
(b) Both rinses were at 45 sec conversion coating step was skipped.

consumption, make-up and waste disposal rates that need to be verified during the technology development to produce a comprehensive evaluation.

Design Basis

A standard 1892-L (500-gal) tank was used for all process steps to accommodate an assumed size workpiece. This simplified the preliminary design assessment and economics while recognizing that some operations may require different capacities and production rates to be addressed in subsequent iterations of the Engineering Assessment.

The following assumptions were used in this evaluation:

1. Metal surface treatment shop operates 8 hours per day and 5 days per week for 2,080 hours per year.
2. The use of Picklex® does not require changing the composition or operation of the plating bath(s) or subsequent surface finishing operations.
3. Comparable product quality is achieved with each comparison of conventional processing and the Picklex® alternative process.
4. The following chemical costs are used:
   - Hydrochloric acid, 37% HCl, $72/ton.
   - Sodium hydroxide, USP pellets, $1.70/lb.
   - Proprietary aluminum cleaner†, as used, $10/gal.
   - Chromate conversion coating, $10/gal.
   - Picklex® as used, $40/gal.
5. The chemical consumption and make-up rates are as follows:
   - Alkali cleaner is replaced every 6 months (2,500 lb NaOH/yr)
   - Picklex® is replaced every 12 months (500 gal/yr)
   - Pickling solution is replaced every 6 months (10,000 lb HCl/yr)
   - Rust remover is replaced every 6 months (10,000 lb/yr)
   - Aluminum cleaner is replaced every 6 months (1,000 gal/yr).
6. Use of Picklex® solution can replace both the alkali cleaning and the chromate conversion coating in the surface preparation of aluminum for powder coating applications.
7. Waste disposal cost of replacing the chemical baths to averages $0.50/lb.
8. Only one operator is needed for each line.
9. Operator's wage is $20/h.
10. Workload is consistent throughout the year.

Chromate Conversion Coating on Aluminum

Figure 2 illustrates the sequential process steps for both conventional chromate conversion coating on aluminum and the alternative Picklex® process. As shown, the use of Picklex® (Al-P-R-N-N-PC) replaces both the pretreatment (alkali cleaning, two rinse steps, etch, three rinse steps, deoxidizer, two rinse steps) and chromate conversion coating (chromate conversion coat and three rinse steps).

The revised capital cost savings associated with eliminating these process steps and associated equipment are estimated to be $254,000 because of the decreased number of process steps. Using the same factored cost estimate of Phase I that includes piping, installation, electrical, instrumentation and controls, utilities and other services the cost savings was calculated. Table 7 provides detailed cost elements that were estimated in the engineering assessment.

Additional savings are not included for incremental cost of building/floor space, water treatment and ventilation. These additional savings could be significant for a new facility (Greenfield site) or a total facility refurbishment that included these ancillary components, especially if the freed-up space enabled additional production capacity to be brought on line. Also, since this study the price of Picklex® has dropped.

Overall, the operating costs for conventional pretreatment of aluminum are $46,000 higher than the alternative Picklex® process. Table 8 presents the estimated operating cost savings, including the direct labor costs based on the process time needed at Mills. The assumptions included only one operator at an hourly wage is $20, with the workload consistent throughout the year. The process time not including degreasing, drying and powder coating (times are the same for both commercial and Picklex® processes) is 20 minutes for pretreatment and chromate conversion coating on aluminum and one minute for processing with Picklex® as the pretreatment and conversion coat. The chemical costs remained the same as Phase I. Consistent with Phase I, both conversion coating processes would have the same powder top coating operations and costs.

Table 6
Comparison of Commercial Partner No. 1's Production Samples Versus Picklex® Treated Samples (Batch 3)

Sample Type	Adhesion Rating
Production Samples from Commercial Partner No. 1	0B-2B
DDD Picklex® Rinse (45 sec) plus Chromate	4B
EEE Picklex® Rinse (45 sec)	3B-4B(a)
FFF Picklex® Quick Rinse	4B

(a) Only one sample received 3B rating. The remaining samples received 4B rating.

***** *Spraylat PEB1867C, Spraylat Corp., Mt. Vernon, NY.*

Table 7
Capital Cost Savings

Cost Element	Commercial Pretreatment & Chromate on Aluminum	Commercial Pretreatment & Zinc Phosphating on Steel
Tank	$27,000	$15,000
Spill Containment	$1,500	$750
Pump	$26,000	$26,000
Filter	$7,200	$7,200
Mixer	0	0
Heater	$8,000	$6,000
Power Supply	0	$8,000
Subtotal PEC	$69,700	$62,950
Installation (30% PEC)	$21,000	$19,000
Piping (30% PEC)	$21,000	$19,000
Instrumentation (10% PEC)	$7,000	$6,300
Electrical (10% PEC)	$7,000	$6,300
Utilities		
Engineering (33% PEC)	$23,000	$21,000
Contingency (50% PEC)	$35,000	$32,000
Working Capital		
Total Capital Savings	$254,000	$230,000

Empty cells indicate cost element was not estimated.
PEC = purchased equipment cost.

compared to production samples from Commercial Partner No. 1. Further testing is recommended to validate these results on a production scale.

Pencil Hardness

ASTM D3363 (*Standard Test Method for Film Hardness by Pencil Test*) describes a procedure for rapid, inexpensive determination of the film hardness of an organic coating on a substrate. It was used here as a quality control check much like a dry film thickness test. The powder coatings used in this study were in the hardness range of HB to 3H with no discernable difference from substrate to substrate or scenario to scenario.

Impact

Impact testing was another way to evaluate adhesion. The field testing replicated the laboratory tests. Phase II achieved additional promising results for both aluminum and steel. For aluminum, Phase I showed that impact adhesion between conventionally pretreated panels and Picklex® pretreated panels was equivalent. Table 5 shows the average impact results for each group and the panels which failed impact adhesion. Group A had one failure, A6, showing that Picklex® pretreated panels had slightly higher impact resistance than conventionally pretreated panels for aluminum. Impact resistance results showed that Picklex® can at least serve as a mild degreaser for steel, comparing group BB's average of 155 to group CC's similar average of 158 (both groups are defined in adhesion by tape section). Also, the comparison between groups F and S for aluminum and M and BB for steel show that the results are consistent.

Certain groups of aluminum panels from Batch No. 1 and 2 failed the impact adhesion test at 5.42 J (4.0 ft-lbs). All of the groups that were powder-coated with another powder coat material for aluminum**** failed the test except for Group X which received very low passing results. These results suggest that the powder coat material and not the pretreatment or conversion coating caused the failures. Further, Groups Y and Z, which did not receive a rinse after Picklex® failed the impact adhesion test at 5.42 J (4.0 ft-lbs). These results show that at least a quick rinse is needed after processing in Picklex®.

Bend

The mandrel bend test was another way to evaluate adhesion. Results for bend tests for Batch Nos. 1, 2, and 3 are listed in Table 5. In Phase II, pretreatment rather than top coating was being investigated. Therefore, ASTM D 522 was modified with respect to the definition of pass/ fail. In this study, visible cracking was not a "fail" unless coating was removed by pressure-sensitive tape at the cracking site. Failure was defined as loss of coating adhesion.

Corrosion

Corrosion testing used exposure in a salt fog chamber following ASTM B 117 (*Standard Practice for Operating Salt Spray Apparatus*). Powder coated panels were scribed with an X, protected by tape on the edges and exposed in a standard salt spray cabinet for periods up to 1760h. All panels were inspected at 200h for signs of corrosion and returned to the salt spray cabinet for continued exposure. Table 5 shows the results. The length of salt fog exposure was determined by time of processing and project end date. Batch No. 1 test panels were observed to 1760h. Batch No. 2 test panels were observed to 1277h, while those for Batch No. 3 were observed to 144h. The failure point was defined for this study as loss of adhesion. Pressure-sensitive tape was placed over the scribed area on the dried panel and removed. If coating was removed with the tape, the panel failed.

Aluminum panels from Batch Nos. 1, 2, and 3 did not display loss of adhesion due to corrosion within the time frame of this study (1760h). More recent tests[7] showed no corrosion up to 2800h with a goal of 4000h. Steel panels from Batch No. 1 did not show loss of adhesion until 1376h. This compares with similar panels from Batch No. 2, which showed loss of adhesion by 608h.

In comparing groups A versus B and J versus K (all groups from Batch No. 1), we found that the salt fog results show that the laboratory process test results were verified in the field. During Phase I and II, equivalent corrosion resistance was noted when comparing commercially pretreated panels versus Picklex® pretreated panels.

Engineering Assessment

The objective of this assessment was to evaluate a preliminary engineering design and its economics to guide subsequent development and potential commercial implementation. Both capital and operating costs were estimated as incremental costs relative to the conventional processes. The capital cost estimates were based on orders of magnitude and include 50% contingency because of the limited design detail available and the uncertainties of a general evaluation as opposed to site and application specific. Based on the commercial operation information obtained at Mills, the engineering assessment was revised to include commercial practice and potential labor savings. Several assumptions were included about

Table 8
Operating Cost Estimate

Cost Element	Unit Cost	Conventional Process		Picklex® Process	
Chromate on Aluminum					
Chemicals		Quantity	Annual Cost	Quantity	Annual Cost
Alkali Cleaner	$1.70/lb	2,500 lb	$4,250/yr		
Aluminum cleaner (a)	$10/gal	1,000 gal	$10,000/yr		
Chromate	$10/gal	1,000 gal	$10,000/yr		
DI Water	$0.05/gal	10,000 gal	$500/yr	500 gal	$25/yr
Picklex®	$40/gal			500 gal	$20,000/yr
Waste Treatment	$0.50/lb	12,000 lb	$6,000/yr	5,000 lb	$2,500/yr
Direct Labor	$20/hr	2,000 hr	$40,000/yr	100 hr	$2,000/yr
Maintenance					
Operating Supplies					
Utilities					
Analytical Lab					
Fixed Costs					
Indirect Costs (OH)					
Subtotal			$70,750/yr		$24,525/yr
Indirect Costs (OH)					
Subtotal			$70,750/yr		$24,525/yr
Zinc Phosphating on Steel					
Chemicals		Quantity	Annual Cost	Quantity	Annual Cost
Alkaline cleaner (b)	$4.91/gal	1,000 gal/yr	$4910/yr		
HCl	$72/ton	5 ton/yr	$360/yr		
Zinc phosphating compound	$7.05/gal	1,000 gal/yr	$7,050/yr		
DI Water	$0.05/gal	10,000 gal	$500/yr	500 gal	$25/yr
Picklex®	$40/gal			500 gal	$20,000/yr
Waste Treatment	$0.50/lb	10,000 lb	$5,000/yr	5,000 lb	$2,500/yr
Direct Labor	$20/hr	2000 hr	$40,000/yr	170 hr	$3400/yr
Maintenance					
Operating Supplies					
Utilities					
Analytical Lab					
Fixed Costs					
Indirect Costs (OH)					
Subtotal			$58,000/yr		$26,000/yr

Empty cells indicate that cost element does not exist.
(a) Alumiprep® 33, Henkel Surface Technologies, Madison Heights, MI.
(b) Aeroclean DN-30, ONDEO Nalco Company, Naperville, IL.
(c) Aerocote #3, ONDEO Nalco Company, Naperville, IL.

Zinc Phosphating on Steel

Figure 1 illustrates the process steps for both conventional zinc phosphating on steel and the Picklex® process. Picklex® replaces the pretreatment (electrocleaner and one rinse step) and conversion coating (conversion coat and three rinses).

The capital cost savings, shown in Table 7 is estimated to be $230,000 using the same factored cost estimate as Phase I which includes piping, installation, electrical, instrumentation and controls, utilities and other services. The revised capital cost savings results from the reduced number of steps between Mills' process and the Picklex® alternative. As previously stated, additional savings are not included for the incremental cost of building/floor space, water treatment, and ventilation.

The operating cost savings, presented in Table 8 include the direct labor costs. Using the assumptions described in the chromate conversion cost estimate, the direct labor costs for using zinc phosphate are $36,600 higher than using Picklex®. The estimated time for processing one load through the zinc phosphate line is 25 minutes compared to the 2-min process time for Picklex® with steel.

Results & discussion

Several qualitative processing advantages of Picklex® were found during Phase I, which include adequate draining time, easy agitation and slow evaporation rate. An extended bath use period test was performed during Phase I, which showed that the bath did not form solids with use, and that Picklex® operates at ambient temperature. These advantages of Picklex® were confirmed during Phase II.

† *Alumiprep® 33, Henkel Surface Technologies, Madison Heights, MI.*

The field testing at Mills showed that the use of Picklex® reduced the number of process steps considerably compared to commercial processes. The optimum Picklex® process for aluminum and steel that receives a powder coat finish (Fig. 3) may consist of degreasing, Picklex® immersion dip (30 sec for aluminum and 90 sec for steel) and a quick rinse step (in and out). The processed parts may then be dried and powder coated. The commercial processes for both pretreatment and chromate conversion coating for aluminum and pretreatment and zinc phosphate conversion coat on steel include many more process steps (11 more steps for aluminum and five more steps for steel).

A disadvantage of Picklex® is that the near term unit cost is $40/gal. However, the remaining operating and capital cost savings may offset the difference in chemical costs. Picklex® also has a slow evaporation rate and high tolerance to contamination and so does not need to be replaced on a regular basis.

The revised engineering assessment showed the economic impact of using Picklex® as a replacement for chromate conversion coating and zinc phosphating. Both the capital cost savings and the annual operating cost savings are summarized in Table 9.

Table 9
Summary of Cost Reductions of Using Picklex® Instead of Conventional Pretreatments

Cost Reduction	Savings Relative to Chromate on Aluminum	Zinc Phosphating on Steel
Capital Cost Savings	$254,000	$230,000
Annual Operating Cost Savings	$ 46,000	$ 36,600

Recommendations

Steel and aluminum components were evaluated during Phase II. The Picklex® treated aluminum components provided improved adhesion over the current production technique. Based on the positive test results, an application specific field test on aluminum components is recommended.

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