Environmentally Friendly Anticorrosive Primer Based on Oxy-Amino-Phosphate of Magnesia substituting Chemical Pretreatment for Aluminum

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Abstract
Corrosion inhibiting pigments based on oxy-amino-phosphate of magnesia (OAPM) are environmentally friendly, non toxic , zinc and heavy metals free, as well as efficient and proven substitutes for the currently used anti corrosion pigments.

Due to the high effectiveness of OAPM pigments, significantly lower loading is needed in comparison to zinc chromate, basic and modified zinc phosphate, ion exchange pigments and others. This leads to formulation cost effectiveness in addition to the health and environmental advantages.

Following a brief summary of the protection mechanism by OAPM, the present work describes the development of both solvent and water based formulations of anti corrosion primers which were used to substitute a commercial chemical pretreatment for aluminum profiles used in the building industry.
The solvent borne primer was top-coated on an industrial line substituting chromate based and non chromate based standard pretreatments showing excellent performance after 2500 hours in salt spray and humidity standard tests.
The water borne primer also exhibited excellent results, as well as a very good in can stability.

This work demonstrates the feasibility of substitution of the currently used chemical pretreatments by an environmentally friendly, non toxic primer based on OAPM.

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Introduction

Aluminum and its alloys are widely used in many industries such as the building, transportation, food packaging etc. Common examples are: building siding and window profiles, trucks and aircrafts construction and sidings and beverage containers.
In order to protect aluminum surface from corrosion and to improve adhesion of subsequently applied organic coatings, two main types of pretreatments are used according to the specific end use requirements, namely, various types of chemical conversion coatings as well as primer coatings
Schematically, the common factor of these two types of surface treatment, until recently, was the use of chromate compounds as the anti corrosion ingredient, while the basic difference is the use of a polymeric binder in the case of "wash" or "etch" primers while conversion coatings are basically solutions of various ingredients in water.
Chromate conversion coatings (CCC) which react with the metal surface to change its chemical nature provide excellent corrosion protection and adhesion and are still widely used especially in the aerospace industry (1).
Wash primer (WP) which forms a 7 to 10μ film on the metal surface was developed during World War II as a primer for aircrafts aluminum structure and envelope and is prepared according to specification MIL-C-15328.
Typical wash primer contains a chromate compound in a vinyl butyral polymer solution and phosphoric acid as a separate component added just before application. It is believed that first an inorganic film of a chromic phosphate is formed followed by an organic film of the deposited polymer. The polymer reacts with the inorganic film to crosslink and become insoluble (2). This resulting film has excellent adhesion to various metals and excellent performance in corrosive conditions.
A one component version, sometimes called "Etch Primer" was also developed. It is based on the addition of epoxy and phenolic resins to the wash primer formulation while reducing the amount of phosphoric acid.
However, since these treatments contain hexavalent Cr which is a human carcinogen with an extremely low Personal Exposure Limit (PEL) of 1 mg/m^3 (3, 4, and 5), their use is severely restricted by the European and U.S regulation agencies.
Consequently, many nonchromated coating and treatments have been developed and tested over the past several years. See for example references 4, 5 and 6.
Non-Chromate wash primers were also developed and commercialized but must of them contain zinc which is regarded as hazardous to the environment (7).
Corrosion inhibiting pigments based on oxy-amino-phosphate of magnesia (OAPM) (8), offer an environmentally friendly, non toxic, zinc and heavy metals free route to non chromate corrosion protection of aluminum.
OAPM pigments are also cost effective since due to their high effectiveness, significantly lower loading is needed in comparison to other alternatives (9,10)
Previous investigations (11) showed that OAPM pigments have good corrosion protection ability on Al alloys 3105-H24, 6061, 6063 and 2024-T3.
The most important parameter of the protection mechanism by OAPM is the formation of a continuous film, 40 to 100 nm by thickness which is very similar in shape to the layer formed by chromates as observed by HRSEM. This layer is composed of oxidized Mg and P as resulted from Auger (AES) analysis (11).
Electrochemical measurements of scribed panels coated with OAPM containing paints showed that the surface potential of painted aluminum without AC pigment

tends to move quickly into the corrosion zone while an OAPM containing paint, keeps the surface potential below the corrosion values during the test, thus, cathodically protecting the aluminum surface (12).
The present work describes the development of both solvent and water based formulations of OAPM based anti corrosion primers and the feasibility of their use as substitutes for commercial chromate and non-chromate conversion pretreatment coatings.
The solvent borne WP applied on aluminum profiles (AL 6063) used in the building industry was top-coated by commercial polyester-melamine stoving paint on an industrial line substituting standard chromate based and non chromate based pretreatments showing excellent performance after 2500 hours in salt spray and humidity tests.
In another test OAPM based WP was used to prime ALCLAD panels which were top coated with a commercial 2 K polyurethane paint to resisted 2500 hours salt spray and humidity tests.
Excellent corrosion resistance data of water borne OAPM based primer with a very good in can stability are also presented.

Experimental

Materials

A. Substrates

(a) **AL 6063** commercial profiles and panels supplied by Klil Industries, Carmiel, Israel, were used as substrates for the coating tests in the standard production line.
(b) **ALCLAD** aluminum panels received from Akzo Nobel, USA were used for laboratory tests with solvent based OAPM based primers top-coated with 2K polyurethane – acrylic paint.
(c) **AL 3003** panels from Q-Panel Inc., USA, were used for the evaluation of water based OAPM containing primers prepared in the laboratory.

B. Metal Surface Preparation

The chemical surface pretreatment for the AL 6063 and ALCLAD substrates was the standard process in use in Klil Industries (designated DE), namely:
- Degreasing- etching with Ridoline 34®, 1.5% and Ridosol 521®, 0.2% (dipping for 4-6 minutes @ 65-70ºC).
- Desmutting with Deoxidizer HX 357® for 4-6 minutes @ RT
- The standard chemical conversion coatings of the production process used as a reference for the performance of the OAPM based primers were chromate based Alodine 713 and non-chromate Alodine 4830/4831.

.All of the mentioned materials are products of Henkel Surface Technologies, Germany. For all WP coated panels and profiles the DE process was reproduced in Pigmentan laboratory
In the case of ALCLAD an additional set of panels was pretreated by solvent cleaning alone using Methyl Ethyl Ketone (MEK).

AL 3003 panels were primed without any pretreatment.

C. OAPM based primers

(a) Binders

The main binder for the solvent borne wash primer formulations was poly-vinyl butyral (Mowital 30H, and 60H, produced by KSE GmbH, Germany).

In the etch primer formulations epoxy and phenolic resins were included. (Beckopox E301/75X and Phenodur PR 263/55B which are products of Cytec Surface Specialties.).

For the water borne primer, three styrene acrylic emulsions were used as the binder, namely, Neocryl XK 87 of DSM, The Netherlands, Worléecryl 7120 of Worlée Chemie GmbH, Germany and Maintcote PR 71 of Rohm & Haas, USA.

(b) Anticorrosion Pigments

The OAPM anti corrosion pigments used in this work were:

- Pigmentan E
- Pigmentan 465M
- Pigmentan EA for the water borne formulations.

All are products of Pigmentan Ltd. Ramat Gan, Israel.

The water based primer development included for reference , Heucophos ZCP, a modified zinc phosphate anti corrosion pigment made by Heubach, Germany.

D. Top-Coats

In the laboratory tests a commercial 2K acrylic-polyurethane solvent based paint was used (Unicryl®, a product of Nirlat, Kibutz Nir-Oz, Israel).

In the factory line application, the standard topcoat used by Klil Industries namely, BecryPol E® Stoving Paint, was used. It is a polyester-melamine formaldehyde paint, a product of Beckers Industrielack GmbH, Germany.).

Preparation, Application and Test Methods

Wash primer formulations with various combinations of the OAPM AC pigments and binders were prepared by dispersing to a Hegman value higher than 6 with a saw tooth impeller driven by a high speed stirrer using glass beads , 2-3 mm in diameter, as the dispersing media.

The solvent and water based formulations developed in this work are detailed in **Table** 1 and 2, respectively.

Table 1: OAPM Solvent Based Primer Formulations

	supplier	WP-5	PMN402/05	PMN402/06
Mowital Solution A 14%			68	68
Mowital Solution B. 10%		74		
Texaphor Special	Cognis	0.4		
Araldite 7071 Sol 50%	Huntsman	3.7		
Phenodur PR263 55% in butanol	Cytec		4	4
Beckopox EP 301 75%	Cytec		3.7	3.7
MIX WELL and ADD				
PIGMENTAN 465M	**Pigmentan**	**3**	**2.90**	**-**
PIGMENTAN E	**Pigmentan**		**-**	**2.5**
Talc IT Extra	Norwegian	1.5	5	5
Aerosil 972 10% paste in Xylene	Degussa		3.3	3.2
Aerosil 200	Degussa	0.5		
GRIND TO HEGMAN 6 and ADD				
Butanol		15		
Solvent PM	Dow		3	3
Xylene			7	7.5
MIX WELL and ADD				
Phosphoric acid 85%/Butanol 1:3		1.85	3.2	3.2
TOTAL		**100.0**	**100.1**	**100**
Mowital Solution A 14%		%WT		
B60 H Mowital	KSE	7.0		
B30 H Mowital	KSE	7.0		
Butanol		56		
Propanol		30		
Mowital Solution B. 10%				
B30 H Mowital	KSE	10		
Butanol		45		
Propanol		45		

Table 2: OAPM Water Based Primer Formulations

PART A	Supplier	WB-WP2	WB-WP7	WB-WP8	WB-WP9
Demineralized Water		12	9	9	10.7
KTPP(Potassium Tri-Poly-Phosphate)	B.K.Giulini	0.5	0.5	0.5	0.5
Orotan 731	Rohm & Haas	2			
Orotan 165	Rohm & Haas		2.4	2.4	2.6
Nalzin-FA 179	Elementis	0.4	0.4	0.4	0.4
Butyl Glycol	Dow	4.5	4.5	4.5	4.8
DMEA (Di-Methyl-Ethanol-Amine)		0.1	0.1	0.1	0.1
ZCP	Heubach			**22**	
PIGMENTAN EA	**Pigmentan**	**18**	**18**		**12.9**
Micro Talc IT Extra		4	4	4	4.3
GRIND TO HEGMAN 6 and SLOWLY ADD					
NEOCRYL XK 87,51%	DSM	56			
WORLÉECRYL 7120, 49%	Worlée Chemie		56	56	
MAINCOTE PR 71,50%	Rohm & Haas				60.2
Texanol	Eastman	2	2	2	2.1
Byk 022	Byk Chemie	0.2	0.2	0.2	0.2
Acrysol SCT 275	Rohm & Haas	1	1	1	1.1
TOTAL		**100.7**	**98.1**	**102.1**	**100.0**
PART B (optional)					
Phosphoric Acid 85%,25% in DI WATER		2.35	2.35	2.35	2.35

The primers were applied by a wire applicator to the aluminum panels and by air spraying to the aluminum profiles to a Dry Film Thickness (DFT) of 7-10µ and were left to dry at ambient conditions for at least 1 day before top coating.
Top coating of the panels in the laboratory with a 2K polyurethane Unicryl® paint was done with a wire applicator to an average DFT of 40-50µ.
Top coating and curing of the coated aluminum profiles was carried out in Klil Industries Ltd. Carmiel, Israel by adding the profiles to a regular coating line
At least 4 panels were prepared per formulation. 2 panels were X scribed and evaluated after exposure to the Salt Spray and Humidity standard tests. Average values were recorded.
Corrosion resistance of the tested articles was made by exposure in salt spray (SST) and humidity standard chambers:

<u>Salt Spray Chamber Test</u>

Tests were carried out in Salt Spray Chamber SASS/120, Sheen Instruments LTD, England, situated in Pigmentan Lab, with 5% NaCl solution .Apparatus parameters were checked daily according to Sheen's and ASTM B 117 instructions.

<u>Humidity Chamber Test</u>

Tests were carried out in a saturated humidity chamber situated in Pigmentan Lab, operating at 47ºC.

Evaluations (Rating) of the coated articles and panels with scribe after exposure to salt spray and humidity were made in accordance to Pigmentan method for evaluation of blistering, scribe and surface rusting, where 0 is the best and 5 is the worst rating. Pigmentan method is based on DIN 53 209 and DIN 53210 and is in accordance to ASTM D610 – Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surface (USA).
The resulting rating is the arithmetical average of the 4 individual ratings (0-the best, 5-the worst), of the following:

- General panel rating
- General Scribe rating
- Blistering degree
- Blistering size

In addition, the blistering situation was evaluated according to *ASTM 714- Standard Test Method for Evaluation Degree of Blistering of Paints* and recorded separately. In this test 10 is a perfect panel while f, M, D describe few, medium and dense blistering and the digit (9 to1) depicts the relative blister size according to the reference. Average Rating results of the tested panels were recorded

Results and Discussion

(a) Solvent Based Primers

Formulations of these primers are given in Table 1.
Formula WP-5 is based on the classical wash primer to which an epoxy resin was added at the level of 25% of the vinyl butyral resin. The inhibiting pigment is Pigmentan 465M. Phosphoric acid solution was added just before application.
Formulations PMN402/05, PMN402/06 follow the pattern of the well known "Etch-Primer" meaning both an epoxy and phenolic resins are included. The difference between these two formulations is the type of the OAPM corrosion inhibiting pigment used, namely, Pigmentan 465M and E.

Al 6063 profiles and panels

Results for Al 6063 profiles and panels coated in the laboratory with OAPM based primers and top coated and baked in an industrial coating line are depicted in Table 3. Photographs of the tested articles after about 2500 hours of SST and Humidity are shown in Figures 1 – 4.
It can be seen that performance of standard aluminum profiles coated with all OAPM based primers and topcoated and baked industrially on-line are equal after almost 2500 hours in SST. After 492 hours exposure to humidity, performance of the WP-5 primed profiles equal that of the standard profile while the other OAPM based primed profiles are practically the same with average rating of 0.5 and 9F for blistering.
The standard treated panels with both chromate and non-chromate pretreatments, showed a marginal advantage over the OAPM based primed panels. However their performance was excellent with an average rating of 0.5 and blistering of 9F while WP-5 primed panel equaled the standards in the humidity test. This can be explained by the fact that both Desmutting and primers` application were done manually in the laboratory, increasing the probability of defects and irregularities. It should be noted that the fact that both rating and blistering degree remained constant throughout the tests indicates the capability of the OAPM based primers to heal and protect the exposed metal at the scribes.

Table 3: SST and Humidity rating for AL profiles and panels primed with OAPM Based Primers industrially topcoated in comparison to standard pretreated AL profiles and panels

		Average Rating				Blistering (ASTM 714)			
Hours in Salt Spray Test		1008	1512	1992	2492	1008	1512	1992	2492
AL Profile from Klil STD Production	PROFILE	0.5	0.5	0.5	0.5	9F	9F	9F	9F
CR KLIL(Chromate pretreatment)	PANEL	0	0	0	0	10	10	10	10
NC KLIL(NonCr Pretreatment)	PANEL	0	0	0	0	10	10	10	10
WP-5	PROFILE	0.5	0.5	0.5	0.5	9F	9F	9F	9F
WP-5	PANEL	0	0.5	0.5	0.5	10	9F	9F	9F
PMN402/05	PROFILE	0	0.5	0.5	0.5	10	9F	9F	9F
PMN402/05	PANEL	0.5	0.5	0.5	0.5	9F	9F	9F	9F
PMN402/06	PROFILE	0.5	0.5	0.5	0.5	9F	9F	9F	9F
PMN402/06	PANEL	0.5	0.5	0.5	0.5	9F	9F	9F	9F
Hours in Humidity Test		1008	1512	1992	2492	1008	1512	1992	2492
AL Profile from Klil STD Production	PROFILE	0	0	0	0	10	10	10	10
CR KLIL(Chromate pretreatment)	PANEL	0	0	0	0	10	10	10	10
NC KLIL(NonCr Pretreatment)	PANEL	0	0	0	0	10	10	10	10
WP-5	PROFILE	0	0	0	0	10	10	10	10
WP-5	PANEL	0	0	0	0	10	10	10	10
PMN402/05	PROFILE	0.5	0.5	0.5	0.5	9F	9F	9F	9F
PMN402/05	PANEL	0.5	0.5	0.5	0.5	9F	9F	9F	9F
PMN402/06	PROFILE	0.5	0.5	0.5	0.5	9F	9F	9F	9F
PMN402/06	PANEL	0.5	0.5	0.5	0.5	9F	9F	9F	9F

Figure 1: Al 6023 profiles after 2492 hours in SST

Figure 2: Al 6023 profiles after 2492 hours in Humidity test

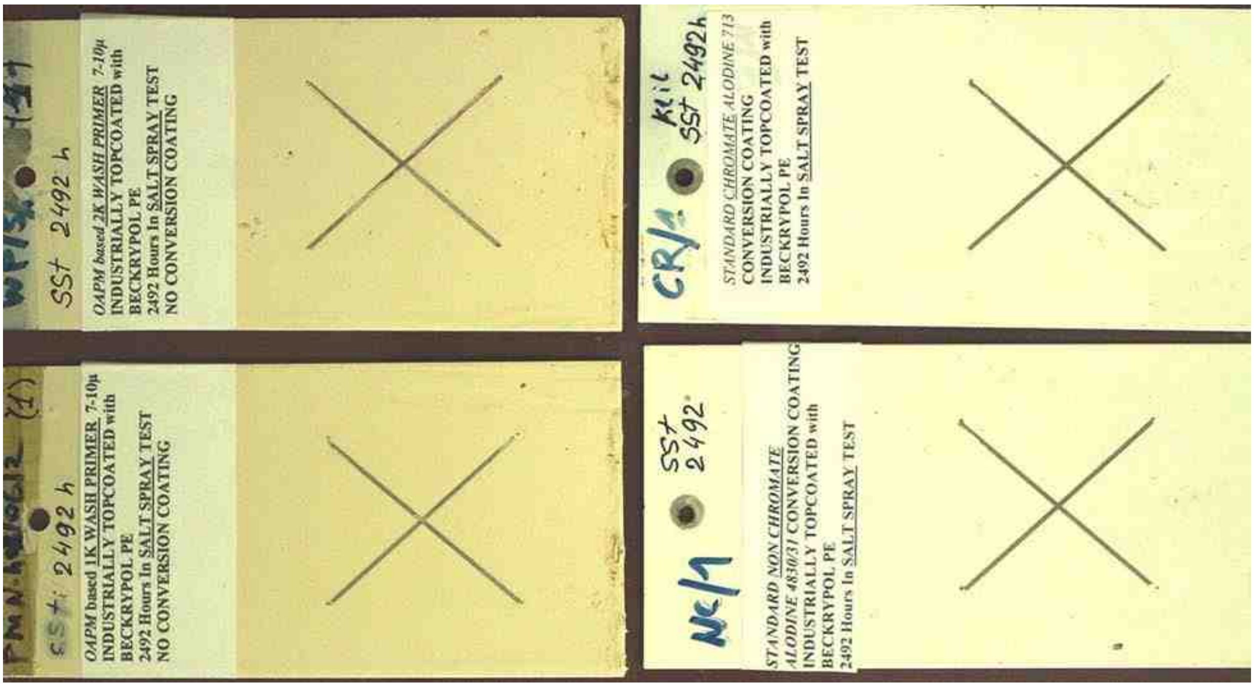

Figure 3: Al 6063 panels after 2492 hours in SST.

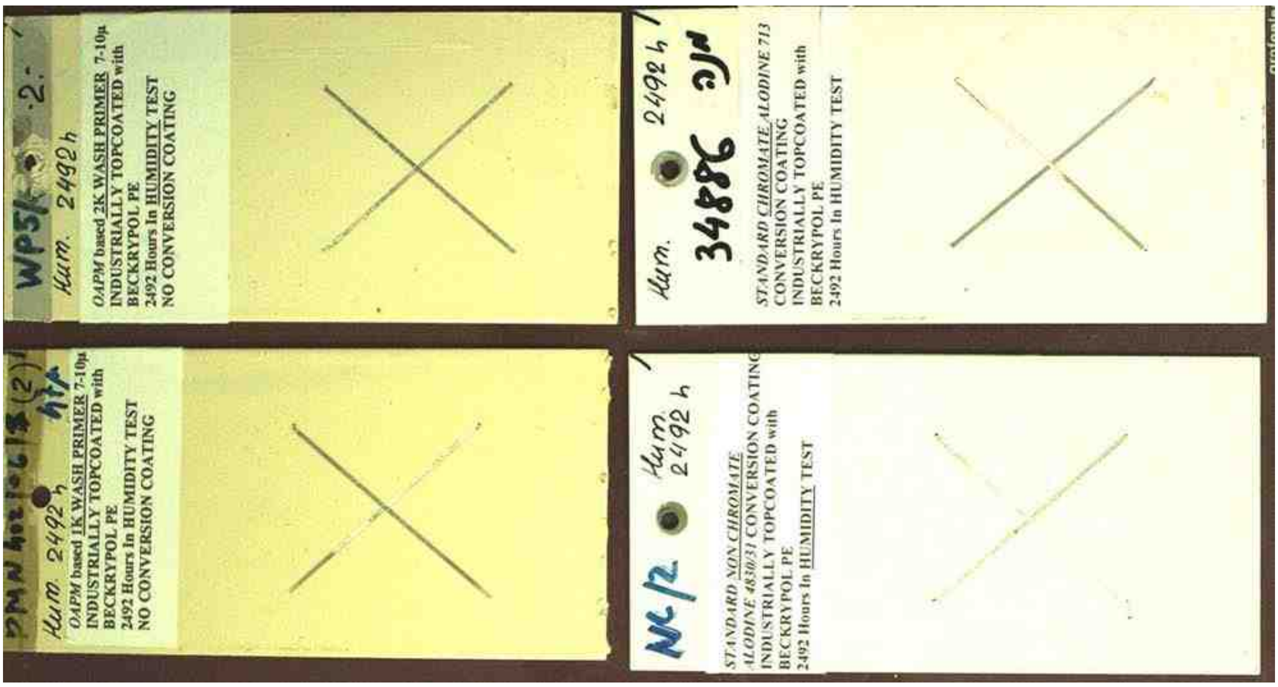

Figure 4: Al 6063 panels after 2492 hours in Humidity chamber.

ALCLAD panels

Results for the ALCLAD panels coated in the laboratory with OAPM based primers and top coated with a commercial 2K acrylic-polyurethane paint are shown in tables 4 and 5 and in figure 5.

In this study, two pretreatments were used, namely, Solvent cleaning with methyl-ethyl ketone (MEK) and the full DE chemical pretreatment which is the standard process in industrial processes. The practical difference between these two pretreatments is obvious.

The SST (table 4) resulted with an average rating is 2 for all primers and pretreatments tested for the primer + top-coat parts of the panels. For the primer alone parts there is a distinct advantage to primer PMN402/05 with a rating o 0.75.

Considering the blistering situation for the top-coated parts of the panels, WP-5 on a MEK treated panels and PMN402/05 with DE treatment are marginally better (9F) than PMN402/06 primed panels (8F). In the primer alone parts of the panels showed a little, PMN402/05 is once again the best with MEK treatment (9F)

In the humidity test (table 5), PMN402/05 and PMN402/06 are better than WP-5 primer with an average rating of 0.5 and 0.75. The blistering situation is the same (9F) excluding the MEK treated WP-5 primed panels with 9FM blisters.

It should be noted that the results indicate an excellent performance of the primers on ALCALD even with a simple pretreatment as the MEK cleaning is.

The differences found are not significant given the variability of the laboratory application and the fact that corrosion resistance of the panel in this study remained practically constant throughout the 2000 hours tests.

Table 4: Average General Rating and ASTM D714 marking after *Salt Spray test* with MEK and DE Pre-treatment *ALCLAD Panels* primed with OAPM Based Primers and top coated with 2K-PU. (Average results)

PRIMER	CONFIGURATION	Pre-treatment	Average Rating		Blistering (ASTM 714)	
			1008hrs	2016hrs	1008hrs	2016hrs
WP-5	WP+TOP		1	2	9F	9F
	WP	MEK	1.5	2.25	9FM	9FM
WP-5	WP+TOP		1	2	9F	8F
	WP	DE	2	2	9FM	9FM
PMN-405-5	WP+TOP		1	2	9F	8F
	WP	MEK	0.75	0.75	9F	9F
PMN-405-5	WP+TOP		1	2	9F	9F
	WP	DE	0.75	0.75	9FM	9FM
PMN-405-6	WP+TOP		1.5	2	8F	8F
	WP	MEK	1	1	9M	9M
PMN-405-6	WP+TOP		1	2	8F	8F
	WP	DE	0.75	0.75	9FM	9FM

Table 5: Average General Rating and ASTM D714 marking after *Humidity test* with MEK and DE Pre-treatment *ALCLAD Panel* primed with OAPM Based Primers and top coated with 2K-PU. (Average results)

PRIMER	CONFIGURATION	Pre-treatment	Average Rating		Blistering (ASTM 714)	
			984hrs	1992hrs	984hrs	1992hrs
WP-5	WP+TOP		1	1.5	9M	9M
	WP	MEK	1	1.5	9M	9M
WP-5	WP+TOP		0.5	1	9F	9F
	WP	DE	0.5	0.5	9F	9F
PMN-405-5	WP+TOP		0.5	0.75	9F	9F
	WP	MEK	0.5	0.5	9F	9F
PMN-405-5	WP+TOP		0.5	0.5	9F	9F
	WP	DE	0.5	0.5	9F	9F
PMN-405-6	WP+TOP		0.5	0.75	9F	9F
	WP	MEK	0.5	0.75	9F	9F
PMN-405-6	WP+TOP		0.5	0.75	9F	9F
	WP	DE	0.75	0.75	9F	9F

(a) **(b)**

Figure 5: ALCLAD panels primed with PMN402/05-OAPM based primer and top-coated with 2K PU paint. (a) After 1992 hours in Humidity test. (b) After 2016 hours in SST.

(b) Water Based Primers

Results for the AL3003 panels coated in the laboratory with OAPM water based primers and top coated with a commercial solvent based 2K acrylic-polyurethane paint are shown in table 6 and in figure 6.

Formulations

.The formulations shown in table 2 are the results of extensive development work aimed at the design of stable formulations with emulsion binders. These binders are known to be sensitive to any deviation from the electrolytic equilibrium that occurs during production if high or low pH ingredients are added.

It was found that using KTTP (Potassium Poly Phosphate) along with careful selection of the wetting agents/dispersants lead to practically stable paints. The formulation presented here based on the three common styrene acrylic emulsions ,

namely, Neocryl XK 87 of DSM, The Netherlands, Worléecryl 7120 of Worlée Chemie GmbH, Germany and Maintcote PR 71 of Rohm & Haas, USA were tested and found to have very good storage stability.
Otherwise, the formulations follow the well known pattern of emulsion based metal primers.
OAPM loading with Pigmentan EA grade, which is specially designed for water based systems, is rather high due to the thin layer of the primers (7-10μ), following the original wash primer thickness specification. Two loading levels were tested. The lower loading was compared to a commercial modified zinc phosphate anti-corrosion pigment on an equal volume basis (formulations WB-WP 8 and 9) .
SST Resistance
Results are shown in Table 1 and Figure 6. As the panels wee only half top-coated, salt spray resistance of both the primer alone and the primer and top=coat system can be evaluated.
The best SST resistance, both rating and blistering, for the primer alone is shown by WB-WP9 and WB-WP7A (where diluted phosphoric acid was added just before application) . However, the best system performance (rating and blistering) was achieved by WB-WP2. Slightly behind are the systems with primers WB-WP7A and WB-WP9. All OAPM based system are clearly ahead of the modified zinc phosphate based system.

Table 5: Average General Rating and ASTM D714 marking after *Salt Spray* *test* 0f AL 3003 *Panels* primed with OAPM Based Water Based Primers and top coated with 2K-PU. (Average results)

PRIMER	CONFIGURATION	**Average Rating**		**Blistering (ASTM 714)**	
		936hrs	**1128hrs**	**936hrs**	**1128hrs**
WB-WP2	WB-WP+TOP	*1.25*	*1.25*	*9F*	*9F*
	WB-WP	1.5	1.75	6F	6F
WB-WP7A	WB-WP+TOP	*1.5*	*1.5*	*8F*	*8F*
	WB-WP	0.75	0.75	10	10
WB-WP8	WB-WP+TOP	*2.25*	*2.25*	*4F*	*4F*
	WB-WP	2.25	2.25	8F	8FM
WB-WP9	WB-WP+TOP	*1.5*	*1.5*	*8F*	*8F*
	WB-WP	0.5	0.75	10	10

Figure 6: AL3003 panels primed with **OAPM Based Water Based Primers and top coated with 2K-PU**. After 1128 hours in SST.

Summary

The use of a thin film primer with OAPM pigments as the anticorrosion element in the formulation proved to be equal in performance when top-coated on an industrial coating line, to the standard systems based on both chromate and non-chromate conversion coatings .

Excellent corrosion resistance was demonstrated with these primers also on ALCLAD panels.

More important and encouraging from the ecological aspect are the excellent results with water based OAPM primers prepared with three different emulsions already common in the field of metal priming.

These findings show the feasibility of replacing conventional pretreatments and wash primers for many aluminum alloys with OAPM based primers which are heavy metals, chromate and zinc free pigments so benefiting from their environmental and economical advantages.

Conclusions

OAPM anti corrosion pigments have shown their capability to protect various aluminum alloys from corrosion when used in both solvent and water based primers.
The feasibility of substituting chemical pretreatment for aluminum with OAPM based primers was demonstrated.
By using OAPM an economic and environmentally friendly approach to the pretreatment and corrosion protection of aluminum can be achieved.

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