

## Studies in Accelerated (Predicted) Versus Observed Anticorrosive Performance for Coastal Industrialized Location

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**Summary:** Accelerated test for corrosion protection is an industrially accepted norm. Even though no correlations are claimed by the coating manufacturers or the users, the users specify and manufacturers comply with the specifications. Coating's performance in actual use conditions may be unrelated to its accelerated test results. In this work, visual examinations and Scanning electron microscopy (SEM)/Energy dispersive X-ray (EDX) analysis were used to study accelerated (predicted) versus observed anticorrosive performance for coastal industrialized location. Commercially available coating systems based on epoxy-polyamide/polyurethane (P<sub>1</sub>), epoxy-polyamide/epoxy-amine (P<sub>2</sub>) and alkyd/alkyd (P<sub>3</sub>) formulations were applied on mild steel test panels (4"x 6" sizes). Then accelerated testing (ASTM B-117) and natural exposure testing at marine test site in Karachi, Pakistan was performed. It was found that the accelerated corrosion testing showed much less severity of corrosion compared to natural exposure testing for all the coatings tested. Severe blistering, filiform corrosion, spread of corrosion around the scribe and loss of gloss were noticed in natural exposure testing. SEM micrographs suggested that the accelerated testing did not show surface features similar to those noticed after natural exposure testing. Principal component analysis explained a variance of 99.98%, 99.97% and 99.29% for P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub> coating systems respectively. These results clearly indicate that no correlation exists between accelerated test method ASTM B117 and natural testing carried out at coastal industrialized location. Based on the results it is suggested to follow a more stringent protocol (inclusion of highly corrosive bromide, sulfite and nitrate ions in acidic pH (6 to 6.5) of the salt solution) for coastal industrialized locations.

**Keywords:** Anticorrosive performance, Mild steel, Scanning electron microscopy (SEM)/energy dispersive X-ray (EDX).

### Introduction

Atmospheric corrosion is an important factor responsible for deterioration of metals. This type of corrosion involves aggressive action by the atmosphere which causes deterioration in the properties of metals [1]. Atmospheric corrosion is an electrochemical process [2]. It involves the oxidation of a metal at the anode and reduction of an oxidant at the cathode. The dominant reaction that occurs at cathode is oxygen reduction reaction. The whole process requires the presence of an electrolyte. The electrolyte is responsible for the completion of an electrochemical circuit between an anode and cathode [3-4]. M. Natesan, *et al.* stated that worldwide the overall cost of corrosion is approximately 4-5% of the gross national product and 20-25% of this cost could be avoided by the use of right corrosion technology [5].

Use of coatings is the most effective and economical method of combating atmospheric corrosion [6-9]. Generally there are two methods for testing the anticorrosive performance of coatings i.e., natural exposure testing and accelerated testing [10-

12]. Ideally, both types of testing should produce similar degradation mechanisms [13]. Studies have been carried out all over the world for determining the anticorrosive performance and also for predicting the service life of different coatings by accelerated and natural exposure testing [7, 8, 14, 15]. Few papers reported different service life prediction approaches [16-18]. Others specified that the performance of coatings is strictly related to specific location and meteorological parameters [19-20].

Success of the service life prediction approach is related to the development of accelerated weathering techniques that can be used to identify the weathering stresses which play an important role in the degradation process [21]. For this purpose, it is essential to study a correlation between accelerated (predicted) and observed anticorrosive performance for a specific location.

The environment of coastal industrial cities is rather harsh compared to developed cities in the main land. This is worse in the case of developing

countries. The salt content of the air due to spray drying of water droplets from sea waves, pollution due to automobiles, industries that emit SO<sub>2</sub>, HCl and NO<sub>x</sub> increase the risk of corrosion of several industrial products that are exposed to this environment. Since the manufacturer can specify only the tests that are available in the standards, the coating supplier has little say in modifying the product. In the process, it is the consumer who suffers. In view of the above, there is a need to carry out such studies in different parts of the world to have a clear vision of correlation between accelerated tests for corrosion protection and actual corrosion protection by using organic coatings. So that the user can identify and then latter rectify the causes in order to avoid losses which have an important impact on the economy of the country.

Besides many incongruities, salt spray test is still the most widely used accelerated test. The purpose of this study is two fold. First is to compare the anticorrosive performance of different coating systems by accelerated (salt spray) and natural exposure testing at coastal industrialized location with the help of visual evaluation, gloss measurement, scribe creep measurement and scanning electron microscopy (SEM). And second is the application of the Principal component analysis on the data obtained from energy dispersive X-ray (EDX) analysis in order to study a correlation between accelerated (predicted) versus observed anticorrosive performance.

## Results and Discussion

### Visual Examination

Visual examination of the anticorrosive performance of different coating systems was done according to ISO standards. The parameters assessed were blistering, rusting, cracking, flaking and filiform corrosion. Blistering is the convex deformation that

occur in a coating system due to the detachment of one or more of the component coats. Rusting is the formation of corrosion products of iron or iron-based alloys. Cracking is the rupturing of the coating due to the formation of cracks in it. In flaking coating system peel off from a surface. Filiform corrosion is a thread-like corrosion that occurs on steel, aluminum, zinc, magnesium, and chromium plated nickel under semi permeable coatings in humid environments (between 30 to 95 percent relative humidity).

Table-1 presents the main results of accelerated (salt spray) testing. The P<sub>3</sub> coating system (Mild steel/Alkyd primer/Alkyd topcoat system) with dry film thickness of 185 μm showed considerable rusting along the scribed region after 240 hours. Severe surface rust staining was also observed. However, filiform corrosion was not observed. Similar system testing at natural exposure test site (Table-2) indicated extensive blistering just after 3 months of exposure. After 6 months of exposure, appearance of corrosion products along the scribe may be introduced difficulty in categorizing the blisters and appeared as the major cause of coating delamination from the scribed region. Some surface rust staining was also observed and as a result further exposure was stopped. Cracking was not observed while the degree of flaking at the end of exposure was determined. Natural exposure testing indicated another major failure mode in P<sub>3</sub> coating system was the formation of filaments of filiform corrosion. Both tests (accelerated and natural exposure) indicated failure in form of appearance of corrosion products along the scribe lines with the natural outdoor panels showing a greater degree of corrosion. An additional mode of failure was observed in natural outdoor tested panels. This was the filiform corrosion. Fig. 1 shows the state of scribed region of unexposed, artificially and naturally exposed P<sub>3</sub> coating system.

Table-1: Main results of accelerated (salt spray) testing.

Coating system code	Coating defects after													
	48 hours		72 hours		96 hours		240 hours		320 hours		480 hours		720 hours	
	B	R	B	R	B	R	B	R	B	R	B	R	B	R
P <sub>1</sub>	0	0	0	0	1S <sub>3</sub>	1	2S <sub>3</sub>	1	2S <sub>3</sub>	3	4S <sub>3</sub>	4	5S <sub>3</sub>	5
P <sub>2</sub>	1S <sub>2</sub>	1	1S <sub>2</sub>	1	2S <sub>2</sub>	2	3S <sub>2</sub>	3	4S <sub>3</sub>	5	d	d	d	d
P <sub>3</sub>	3S <sub>3</sub>	2	3S <sub>3</sub>	2	5S <sub>3</sub>	3	5S <sub>3</sub>	5	d	d	d	d	d	d

B: blistering; R: rusting.

S: Size of blister. The coefficient present along with S indicate the density of blisters while the number in subscript indicates different sizes of blisters (2 = smallest size; 5 = largest size).

d: Panels were removed after exposure due to complete failure of coating system.

0: No detected paint defect.

Table-2: Results of visual examination of the anticorrosive performance of different coating systems exposed in natural marine environment.

Coating System Code	Coatings Defects After																											
	3 months (May2006-Aug2006)				6 months (May2006-Nov2006)				9 months (May2006-Feb2007)				12 months (May2006-May2007)				15 months (May2006-Aug2007)				18 months (May2006-Nov2007)							
	B	R	Cr	F	B	R	Cr	F	B	R	Cr	F	B	R	Cr	F	B	R	Cr	F	B	R	Cr	F				
P <sub>1</sub>	0	0	0	NR	1S <sub>4</sub>	1	0	NR	3S <sub>4</sub>	2	0	NR	3S <sub>4</sub>	3	0	NR	4S <sub>4</sub>	4	0	NR	5S <sub>4</sub>	5	0	4(S <sub>4</sub> )b				
P <sub>2</sub>	2S <sub>5</sub>	1	0	NR	4S <sub>5</sub>	3	0	NR	5S <sub>5</sub>	5	1(S <sub>2</sub> )a	5(S <sub>5</sub> )b	d	d	d	d	d	d	d	d	d	d	d	d				
P <sub>3</sub>	3S <sub>3</sub>	3	0	NR	ND	5	0	4(S <sub>5</sub> )b	d	d	d	d	d	d	d	d	d	d	d	d	d	d	d	d				

B: blistering; R: rusting; Cr: Cracking; F: Flaking.  
 S: Size of blister. The coefficient present along with S indicate the density of blisters while the number in subscript indicates different sizes of blisters (2 = smallest size; 5 = largest size).  
 WOPD: Without preferential direction.  
 ND: Blisters were not detected because of severe corrosion along the scribe.  
 NR: Not rated.  
 0: No detected paint defect.  
 a: Surface crack which do not fully penetrate the top coat.  
 b: Type of flaking in which the whole coating system flaked off from the substrate.  
 d: Panels were removed after exposure due to severe corrosion and paint delamination from the scribe region.

The P<sub>2</sub> coating system (Mild steel/Epoxy-polyamide primer/ Epoxy-amine topcoat system) with dry film thickness of 191 μm showed the formation of some blisters and rust after 48 hours of salt spray testing, (Table-1). Further exposure of the coating system was stopped after 320 hours due to considerable blisters and rust along the scribe. Blistering in the coating system was revealed as the main failure mode. Natural exposure testing indicated the appearance of blisters and rust after 3 months of exposure, (Table-2). After 9 months the coating system was removed due to severe corrosion and coating delamination from the scribed region. Coating delamination from the scribed region appeared to be caused by the formation of underlying corrosion products. Both cracking and flaking were observed and rated according to ISO standards. Filiform corrosion was not observed. Fig. 1 shows the state of scribed region of unexposed, artificially and naturally exposed P<sub>2</sub> coating system.

The P<sub>1</sub> coating system (Mild steel/Epoxy-polyamide primer/Polyurethane topcoat system) with dry film thickness of 220 μm showed the appearance of some blisters and little rust after 96 hours of salt spray testing, (Table-1). Further exposure caused increase in blister density and degree of rusting also. After 720 hours maximum degree of blistering and rusting were observed. Regular filiform corrosion was also observed. Salt spray testing revealed filiform corrosion along the scribed lines as the major mode of failure. Similar system testing indicated little blistering and rusting after 6 months of natural exposure test, (Table-2). After 18 months of exposure, maximum density of blisters and highest degree of rusting caused complete failure of coating system. Coating delamination from the scribed lines

was associated with rust filled coating blisters. The second observed failure mode was filiform corrosion. Regular filiform corrosion was observed. Filaments of filiform corrosion appeared perpendicular to the scribed lines. After natural exposure test there was no indication of cracking while the degree of flaking was rated. Fig. 1. shows the state of scribed region of unexposed, artificially and naturally exposed P<sub>1</sub> coating system.

E. Almeida, *et al.* compared the performance of alkyd, epoxy and polyurethane paints on different substrates after various accelerated and natural exposure tests [8]. They reported that the best behavior was observed for polyurethane paint in both natural atmosphere of high corrosivity and also in the accelerated test. They also found that the intermediate behavior was observed for alkyd paint. Results presented in this study also indicate best performance by polyurethane coating however in contrast alkyd coating showed worst performance in both natural and accelerated testing.

It was apparent from the results of this study that the natural exposure testing caused extremely high degradation of all the coating systems tested as compared to accelerated testing. In addition to this, the major modes of degradation in all the coating systems were completely different in accelerated and natural exposure testing. Ideally, degradation modes must be similar during accelerated and natural exposure testing [13]. B.S. Skerry, *et al.* reported that coatings usually degrade by the action of light, air, temperature and water and this could be worsened by the presence of atmospheric pollutants [12]. F. Deflorian, *et al.* concluded that the weathering of coatings depend on meteorological parameters [20].

Table-3 presents the annual mean of different environmental parameters and Table-4 presents the concentration of major pollutants and particulate matter in natural outdoor environment. The windy climate and the nearness of the sea are supposed to be as causes of highest degradation of the coating systems in marine environment. The aggressiveness of natural exposure conditions caused very high degradation of coatings in natural environment and appeared to be a major cause of lack of correlation with the accelerated results.

*Gloss Measurement*

Specular gloss measurements were made for

- a) control (unexposed) coating systems
- b) coating systems artificially weathered using salt spray chamber
- c) coating systems exposed in natural environment.

Table-3: Annual mean of different environmental parameters.

Year	Parameters						
	Tmax °C	Tmin °C	RH at 0000 UTC %	RH at 1200 UTC %	Wind speed at 0000 UTC knots	Wind speed at 1200 UTC knots	Amount of precipitation mm
2006	32.3	22.5	76.8	51.1	3.9	7.7	301.1
2007	32.9	22.2	76.8	49.2	2.5	7.4	465.6

Tmax = Temperature maximum.  
Tmin = Temperature minimum.  
RH = Relative humidity.  
UTC = GMT: Greenwich mean time.

Table-4: The concentration of major pollutants and particulate matter at natural exposure test site (marine).

	SO <sub>2</sub> ppb	NO <sub>x</sub> ppb	CO ppm	CO <sub>2</sub> ppm	Cl <sup>-</sup> ppm	PM <sub>10</sub> µg/m <sup>3</sup>
Minimum	14	22.7	3.2	340	335	120
Maximum	29	39.6	3.7	358	360	142
Average	22.5	33	3.3	347.2	350	128.1

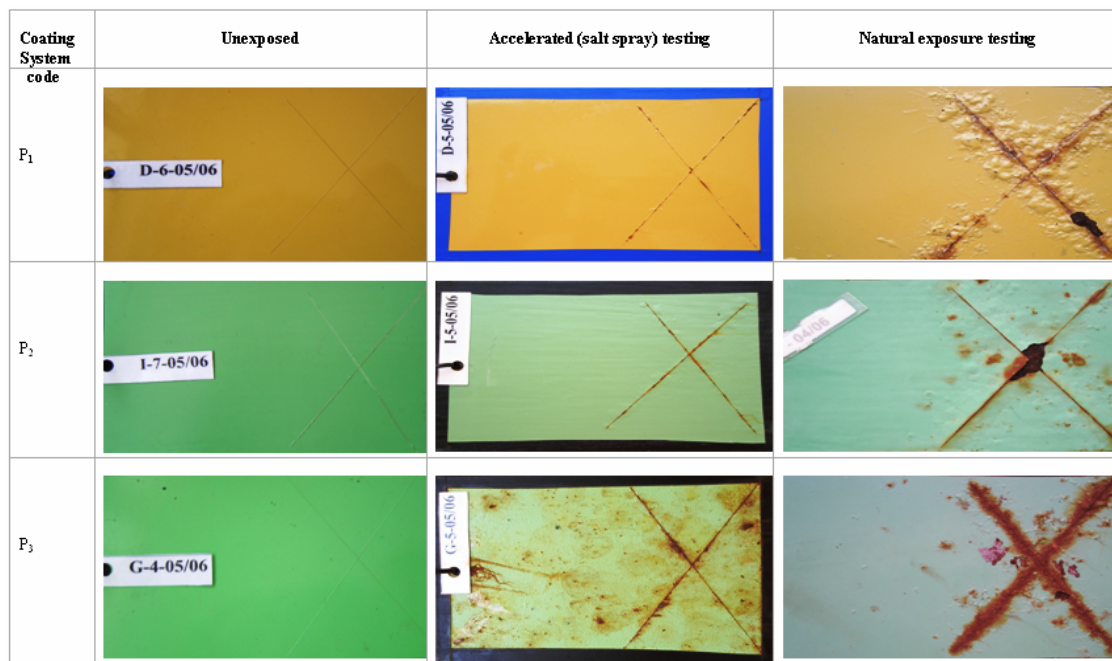


Fig. 1: State of the scribed region of different coating systems after accelerated (salt spray) and natural exposure testing.

Results are shown in Fig. 2. These results show less gloss reduction and likely durability of the epoxy-polyamide/polyurethane coating system (P<sub>1</sub>) in both accelerated and natural environments. These results also suggested that the natural exposure caused severe reduction in gloss in all coating systems as compared to accelerated test performed in salt spray chamber. F.X. Perrin, *et al.* found that the gloss reduction is due to the loss of organic material of the coating [13]. Thus the severe reduction in gloss as a result of natural exposure testing could be related to high degradation of the binder in natural environment. Literature showed that the reduction in gloss of the alkyd coating was reported by F.X. Perrin, *et al.* [22]. V.C. Malshe, *et al.* specified that the aromatic moiety and secondary hydroxyl groups play a vital role in the degradation of epoxy resin [23]. Reduction in gloss of the polyurethane coating was reported by X.F. Yang, *et al.* in their study [24].

*Degree of Corrosion Around the Scribe*

Fig. 3. shows corrosion around the scribe in different coating systems and Table-5 present the results of degree of corrosion around the scribe in different coating systems. It was apparent from these results that the degree of corrosion around the scribe was many times higher in natural outdoor tested

coating systems. M. Morcillo [25] stated that the atmospheric pollution causes the presence of soluble salts within the corrosion products layer which in turn promotes under film metallic corrosion. Thus the high corrosion around the scribe after natural exposure testing could be related to the presence atmospheric contaminants chiefly chlorides.

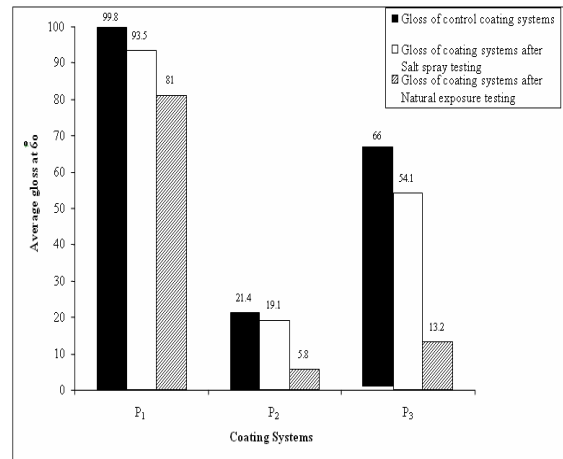


Fig. 2: Comparison of the gloss of different coating systems at °60.

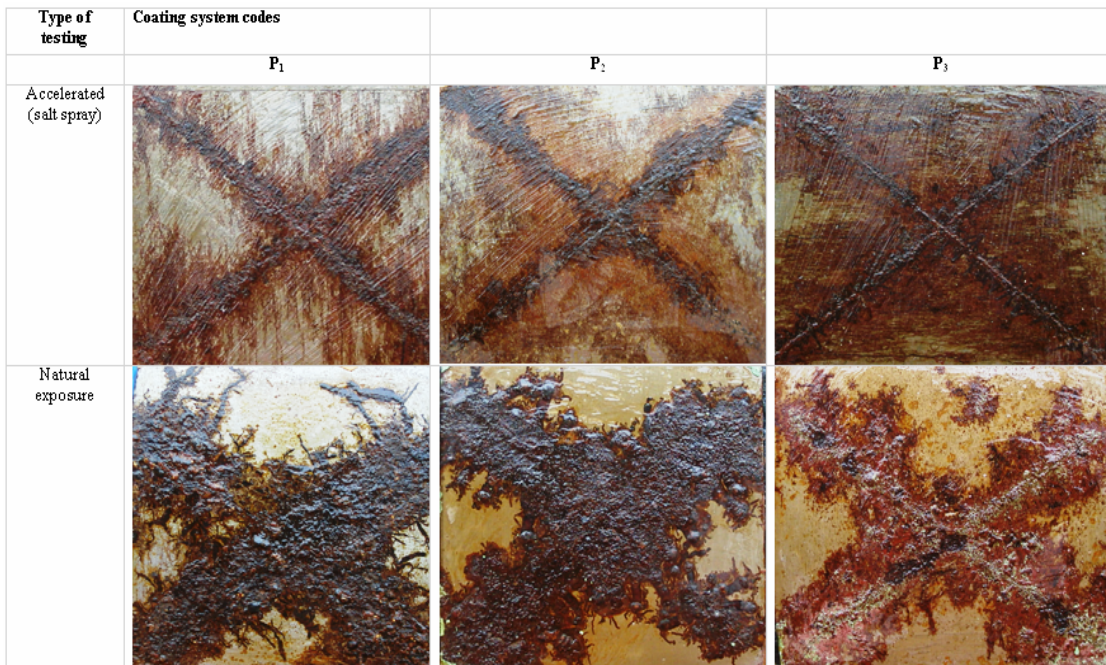


Fig. 3: Corrosion around the scribe in different coating systems after accelerated (salt spray) and natural exposure testing.

Table-5: Degree of corrosion around the scribe after accelerated (salt spray) and natural exposure testing.

Type of testing	Coating systems								
	P <sub>1</sub>			P <sub>2</sub>			P <sub>3</sub>		
	w	w <sub>c</sub>	c	w	w <sub>c</sub>	c	w	w <sub>c</sub>	c
Accelerated (Salt spray)	0.3	2.7	1.2	0.3	2.9	1.3	0.3	2.7	1.2
Natural exposure	0.3	15.3	7.5	0.3	16.9	8.3	0.3	13.1	6.4

w = the width of the original scribe, in millimeters.

w<sub>c</sub> = the mean overall width of the zone of corrosion, in millimeters.

c = the degree of corrosion, in millimeters.

Table-6: Surface composition data of P<sub>3</sub> coating systems as determined by EDX analysis.

Element	Binding Energy keV	Unexposed	Unexposed	Salt spray	Natural exposure
		i mass%	ii mass%	testing mass%	testing mass%
C	0.277	49.42	55.57	47.54	33.09
O	0.525	21.76	33.1	38.71	38.44
Na	1.041	1.81	–	1.04	0.85
Mg	1.253	–	–	–	0.55
Al	1.486	1.06	0.34	0.44	0.92
Si	1.739	0.92	–	0.31	0.9
S	2.307	0.3	–	–	–
Cl	2.621	0.22	0.37	0.34	1.09
Ca	3.69	1.1	0.29	0.9	3.84
Cr	5.411	1.04	–	–	–
Ti	4.508	–	7.05	7.14	13.31
Cu	8.04	0.61	0.64	0.68	–
Zn	8.63	12.66	1.01	0.91	–
Fe	6.398	9.09	1.63	1.99	7.02
Total		100	100	100	100

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analysis

Fig. 4. shows the scanning electron micrographs and corresponding EDX spectra of the surface of P<sub>3</sub> coating system (Mild steel/Alkyd primer/Alkyd topcoat system). The surface of the unexposed P<sub>3</sub> coating system appeared smooth and featureless. Salt spray testing caused less deterioration of the surface of P<sub>3</sub> coating system. In comparison, natural exposure caused considerable changes in the surface morphology of the P<sub>3</sub> coating system. The surface was roughened and large cracks were seen in the micrograph. F.X. Perrin, *et al.* carried out investigation by SEM to study the defects produced in alkyd coating after accelerated and natural exposure testing in marine environment [22]. They found that the SEM micrograph showed less degradation of the surface of alkyd coating as a result of accelerated testing. Results presented in this study for alkyd coating also indicated similar thing. Less degradation in the surface characteristics of alkyd coating was noticed after accelerated testing.

EDX analysis was performed for the unexposed P<sub>3</sub> coating system at two different points on the surface of sample. Results indicated the presence of C, O, Na, Al, Si, S, Cl, Ca, Cr, Cu, Zn and Fe in one EDX spectrum while C, O, Al, Cl, Ca,

Ti, Cu, Zn and Fe in other EDX spectrum taken for the unexposed P<sub>3</sub> coating system [(Fig. 4) and (Table-6)]. The elemental compositions obtained for the P<sub>3</sub> coating systems after accelerated and natural exposure testing is presented in Fig. 4 and Table-6. Chromium was conspicuously absent in the exposed coating systems probably due to its high water solubility. The atmospheric condensation due to high humidity every morning may have washed it off. Similar results are expected in accelerated salt spray testing. In order to study a correlation between accelerated and natural exposure testing, the Principal component analysis (PCA: a Statistical Method) was applied on the data obtained from EDX analysis. Fig. 5. shows loading plots of the Principal component analysis reported the results of the elaborations carried out with EDX data sets obtained for P<sub>3</sub> coating systems. The Principal component analysis of the P<sub>3</sub> coating systems explained a variance of 99.29 % when 2 components were considered. The variance of the first component was explained by the negative and non-significant loadings of the unexposed i, unexposed ii, SST and NET which were not correlated each other. The variance of the second component was explained by the negative and non-significant loadings of the SST and NET, whereas the positive contributions were mainly due to unexposed i and unexposed ii. However, these contributions were also not significant.

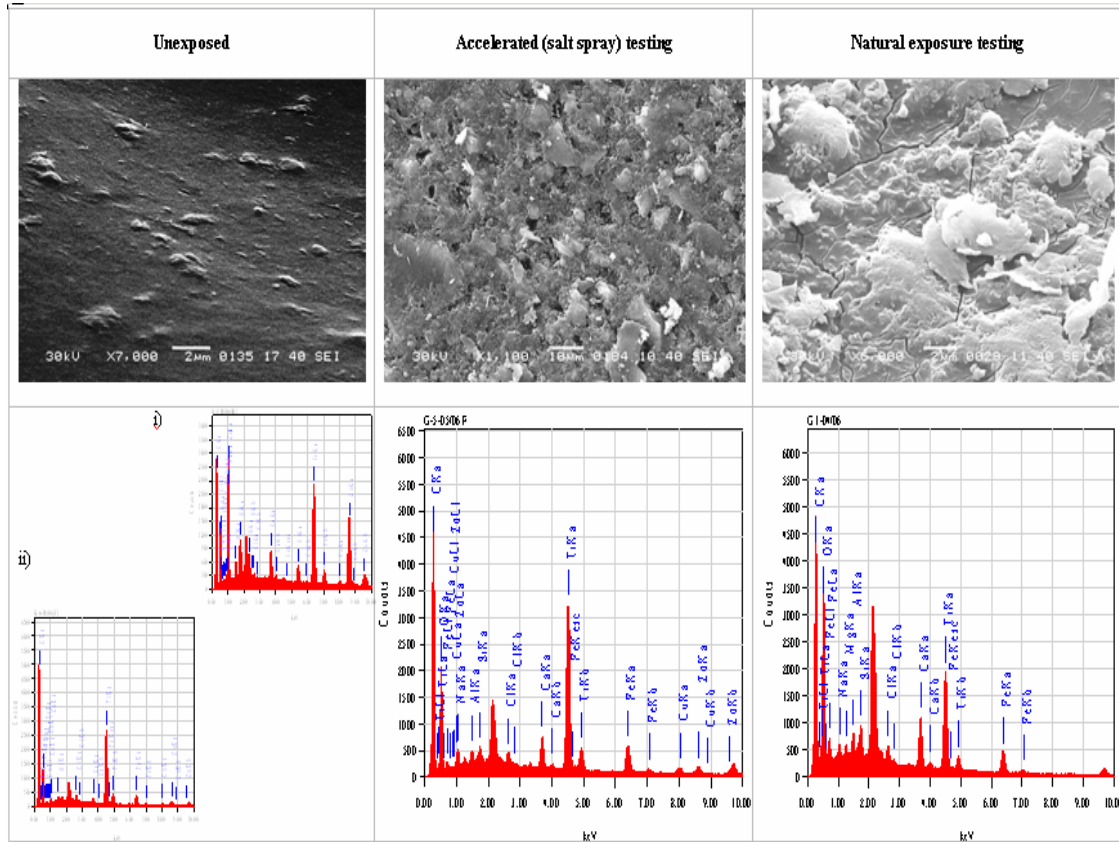
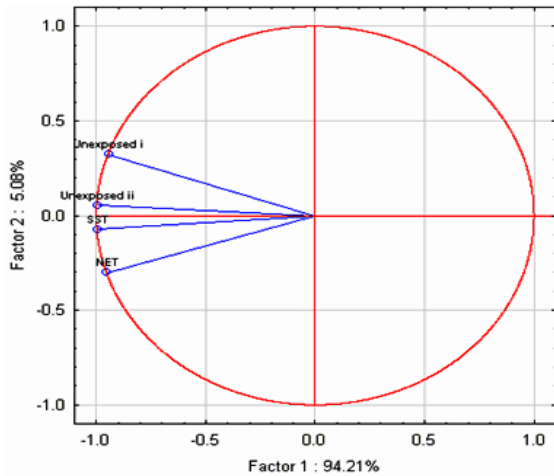


Fig. 4: Scanning electron micrographs and corresponding EDX spectra of the surface of P<sub>3</sub> coating system.



In the axis title of each component the explained variance is reported. Salt spray testing: SST; Natural exposure testing: NET.

Fig. 5: Loading plots of the Principal component analysis reported the results of the elaborations carried out with EDX data sets obtained for P<sub>3</sub> coating systems.

Similar to P<sub>3</sub> coating system, salt spray testing caused less deterioration in the surface characteristics of the P<sub>2</sub> coating system (Mild steel/Epoxy-polyamide primer/ Epoxy-amine topcoat system) and the SEM micrograph showed that the coating surface characteristics, did not appear to be significantly different from the unexposed sample features, (Fig. 6). SEM micrographs also suggested that after natural exposure testing, the coating's surface was severely roughened. The underlying pigment matrix was seen in the micrograph. C. Ocampo, *et al.* compared the resistance of modified and unmodified epoxy coatings against marine corrosion with the help of SEM-EDX [26]. They found that initial regular surface of the epoxy coating was changed to a rough superficial structure after testing. They related the roughening to the appearance of oxides in the polymeric matrix because the EDX analysis revealed an increase in oxygen contents. Results obtained in this study were also consistent with their findings. Smooth surface of the unexposed coating was converted in to rough surface after accelerated and natural exposure testing.

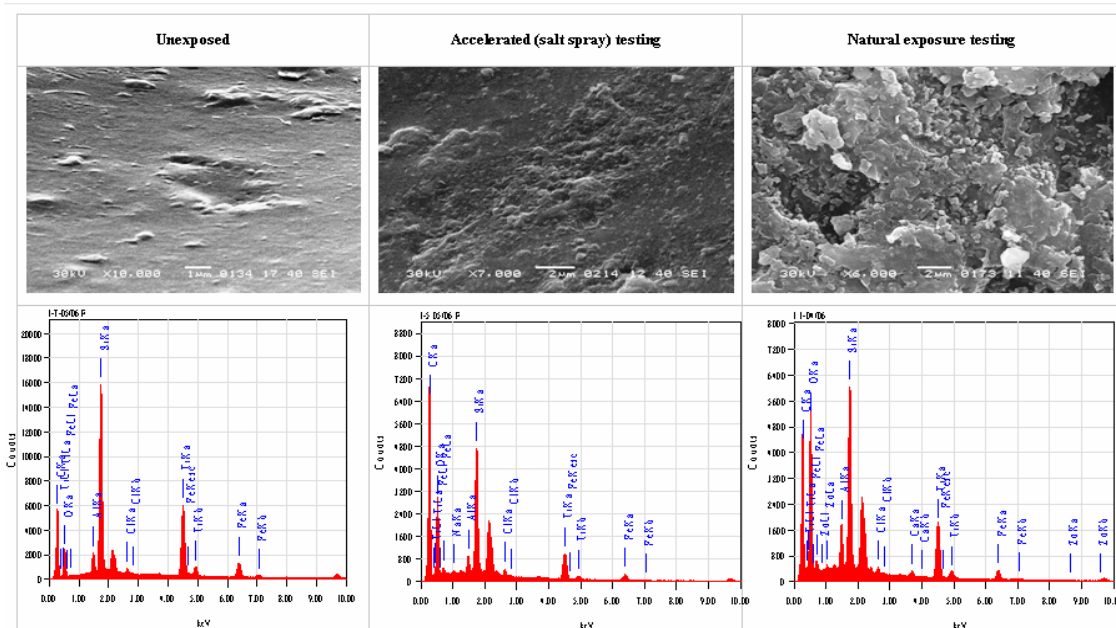


Fig. 6: Scanning electron micrographs and corresponding EDX spectra of the surface of P<sub>2</sub> coating system.

EDX analysis showed the presence of C, O, Al, Si, Ti, and Fe in the unexposed P<sub>2</sub> coating [(Fig. 6) and (Table-7)]. The elemental compositions obtained for the P<sub>2</sub> coating systems after accelerated and natural exposure testing are presented in Fig. 6 and Table-7. Fig. 7. shows loading plots of the Principal component analysis reported the results of the elaborations carried out with EDX data sets obtained for P<sub>2</sub> coating systems. The Principal component analysis of the P<sub>2</sub> coating systems explained a variance of 99.97 % when 2 components were considered. The variance of the first component was explained by the negative and non-significant loadings of the unexposed, SST and NET which were not correlated each other. The variance of the second component was explained by the negative and non-significant loadings of the NET, whereas the positive contributions were mainly due to unexposed and SST. However, these contributions were also not significant.

Table-7: Surface composition data of P<sub>2</sub> coating systems as determined by EDX analysis.

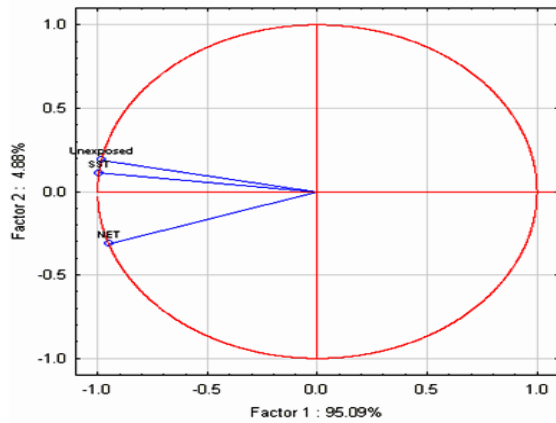
Element	Binding Energy keV	Unexposed mass%	Salt spray testing mass%	Natural exposure testing mass%
C	0.277	52.51	50.22	32.5
O	0.525	26.54	30.13	41.02
Na	1.041	-	0.18	-
Al	1.486	1.31	1.07	2.15
Si	1.739	10.38	8.76	9.93
Cl	2.621	0.31	0.76	0.46
Ca	3.69	-	-	0.52
Ti	4.508	6.63	5.93	9.63
Zn	8.63	-	-	0.01
Fe	6.398	2.32	2.94	3.77
Total		100	100	100

SEM micrograph for the P<sub>1</sub> coating system (Mild steel/Epoxy-polyamide primer/Polyurethane topcoat system) obtained as a result of salt spray testing showed little degradation of the surface when compared with the unexposed coating surface features, (Fig. 8). Similar system testing by natural exposure revealed drastic deterioration of the coating surface characteristics. Surface roughening because of some depositions or structure was observed in the micrograph. Effects of natural exposure testing and different accelerated testing on the surface of polyurethane coating by SEM were reported by C. Merlatti, *et al.* [15]. They found that the surfaces of samples exposed at natural exposure sites were rougher than the surfaces of samples tested by accelerated testing. They also found good correlation between SEM studies and gloss measurements. Results presented in this study were completely consistent with their findings.

EDX analysis indicated the presence of C, O, Al, Pb, Ti, Fe, Cu and Zn in the unexposed P<sub>1</sub> coating system [(Fig. 8) and (Table-8)]. The elemental compositions obtained for the P<sub>1</sub> coating systems after accelerated and natural exposure testing is presented in Fig. 8. and Table-8. Fig. 9. shows loading plots of the Principal component analysis reported the results of the elaborations carried out with EDX data sets obtained for P<sub>1</sub> coating systems. The Principal component analysis of the P<sub>1</sub> coating systems explained a variance of 99.98 % when 2 components were considered. The variance of the first component was explained by the negative and



non-significant loadings of the unexposed, SST and NET which were not correlated each other. The variance of the second component was explained by the negative and non-significant loadings of the NET, whereas the positive contributions were mainly due to unexposed and SST. However, these contributions were also not significant.



In the axis title of each component the explained variance is reported. Salt spray testing: SST; Natural exposure testing: NET.

Fig. 7: Loading plots of the Principal component analysis reported the results of the elaborations carried out with EDX data sets obtained for P<sub>2</sub> coating systems

SEM-EDX analysis is widely employed as a powerful tool for the study of coatings [27-30]. Scanning electron microscopy (SEM) revealed high surface degradation of all the coating systems due to natural exposure testing. EDX analysis as well as the results obtained from PCA indicated lack of correlation between accelerated and natural exposure testing.

Reason for the smooth and featureless surfaces of the unexposed coating systems was well elucidated by B.S. Skerry, *et al.* [12]. They explained that this could be attributed to the formulation of topcoats as a gloss finish systems with a relatively low pigment volume concentration.

X.F. Yang, *et al.* [31] specified the causes for the formation of cracks and increase surface roughening as a result of weathering. According to them, the action of UV radiation, oxygen and humidity on coating material breaks down macromolecules and produce gaseous products, such as carbon monoxide and carbon dioxide, ultimately. Loss of coating material takes place which results in the formation of cracks and pigments erode on the surface.

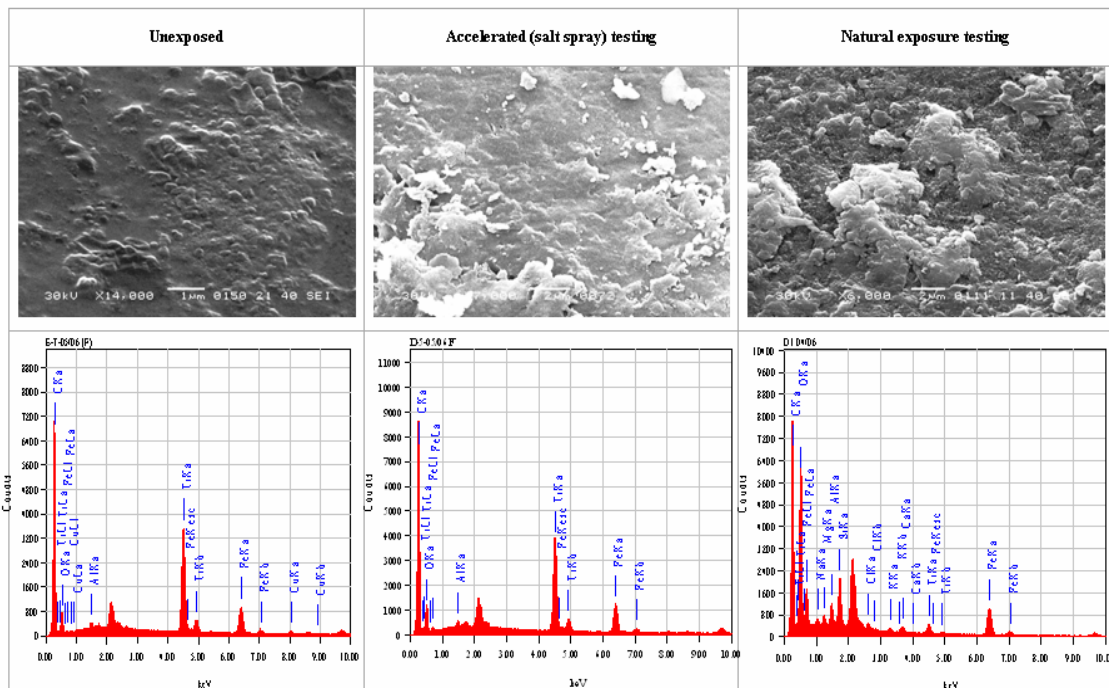
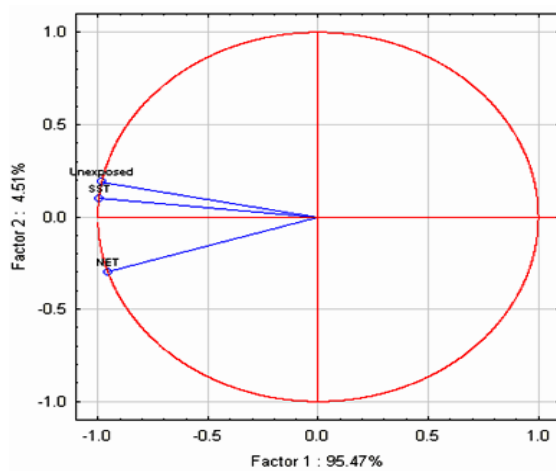


Fig. 8: Scanning electron micrographs and corresponding EDX spectra of the surface of P<sub>1</sub> coating system.

Table-8: Surface composition data of P<sub>1</sub> coating systems as determined by EDX analysis.

Element	Binding Energy keV	Unexposed	Salt spray	Natural exposure
		mass%	testing mass%	testing mass%
C	0.277	63.43	59.48	41.03
O	0.525	23.01	27.7	38.91
Na	1.041	–	–	0.54
Mg	1.253	–	–	0.6
Al	1.486	0.36	0.41	1.26
Si	1.739	–	–	2.56
Cl	2.621	–	–	0.57
K	3.312	–	–	0.32
Ca	3.69	–	–	0.57
Ti	4.508	8.57	7.87	1.63
Fe	6.398	4	4.54	12.02
Cu	8.04	0.63	–	–
<b>Total</b>		<b>100</b>	<b>100</b>	<b>100</b>



In the axis title of each component the explained variance is reported. Salt spray testing: SST; Natural exposure testing: NET.

Fig. 9: Loading plots of the Principal component analysis reported the results of the elaborations carried out with EDX data sets obtained for P<sub>1</sub> coating systems

Sea water contains several other ions, other than sodium and chloride. It is said, sea water has a finite concentration of all the elements present on the earth. Several of these may be corrosive in nature and

some may accelerate the corrosion rates. Bromide ion is one such ion and it is present in sea water in measurable concentration. Industrial atmosphere also contributes sulfur compounds which lower the pH and accelerate corrosion. Hexavalent chromium compounds used in corrosion protecting pigments are partially water soluble and can be easily leached out due to condensation of moisture every morning and the protection is lost. This also makes them environmentally unfriendly. Alternate corrosion inhibiting pigments need to be used for coastal areas. Test methods that include more corrosive components from atmosphere and pollutants need to be included for accelerated testing.

## Experimental

### Test Materials and Specimen Preparation

The material selected as test specimen was mild steel. Mild steel panels with a size of 10 cm x 15 cm (4" x 6") were cut from 1.2 mm thick mild steel sheet provided by Hino Pak Motors Limited (Body Operation Plant). For the surface preparation, mild steel panels were first washed with solvent according to SSPC-SP1 [32], solvent cleaning, to remove grease and oil. This was followed by phosphatizing. Three different commercially available coating systems were selected for the study. After surface preparation specimens were coated with the corresponding coating systems in compliance with the manufacturer's recommendations. Air-operated spray was used for the application of coatings. This was followed by the drying of coated panels in air. Then the dry film thickness measurements were performed according to the method recommended by ASTM D1186 [33] using Elcometer 456 digital coating thickness gauge. A total of 5 measurements were made on each sample at each inspection. The data presented are the average of the measurements. The details of coating systems tested along with their dry film thickness are given in Table-9.

Table-9: Main composition of coating systems tested.

Coating System Code	Primer		Topcoat		Generic Type	Total Average DFT <sup>a</sup> (μm)
	Binder	Pigment	Binder	Pigment		
P <sub>1</sub>	Epoxy-Polyamide	Iron oxide, Zinc phosphate	Aliphatic Polyurethane	Titanium dioxide, Iron oxide	Aliphatic Polyurethane over Epoxy Polyamide	220
P <sub>2</sub>	Epoxy-Polyamide	Iron oxide, Zinc phosphate	Epoxy-Amine	Titanium dioxide, Iron oxide	Epoxy	191
P <sub>3</sub>	Alkyd	Iron oxide, Zinc chromate	Alkyd	Titanium dioxide, Iron oxide	Alkyd	185

<sup>a</sup> = Dry film thickness

The bottom of each dried and cured coated panel was scribed with an X, reaching the base mild steel in order to test resistance to the under film corrosion. The backside and edges of specimen were protected with a tape to prevent premature coating failure.

One set of prepared coated panels was kept as control.

#### *Accelerated (Salt Spray) Testing (SST)*

Accelerated testing was performed according to standard ASTM B-117 [34]. A salt spray chamber was used to provide high humidity (95-98 %) and continuous salt spray (5wt % NaCl) at 35 °C. Prepared coated panels were affixed and orientated at 45° to the normal on plastic racks. Table-2 presents the main results of the accelerated (salt spray) testing.

#### *Natural Exposure Testing (NET)*

One set of prepared coated panels was sent for natural exposure at the marine exposure test site in Karachi, Pakistan. The test site is located adjacent to the Arabian Sea at latitude 24°51'02.63"N and longitude 66°53'08.26"E. Karachi, the city of industries well thought-out as the backbone of the economy of Pakistan is facing the problem of atmospheric corrosion and it can be considered as one of the most suitable sites for carrying out this type of study because of a combination of factors including Marine, Industrial and Urban environments.

Natural exposure testing was carried out according to standard ISO 8565 [35]. At the test site, test specimens (coated panels) were mounted on exposure rack, facing south 45°. Fig. 10. shows the general view of the test site.

#### *Assessment of the Performance of Coatings*

The behavior of the anticorrosive coatings considered in the research led to a number of paint defects. During the visual evaluation of the degradation of the coatings in the scribed region on coated panels the quantity and size of defects and of intensity of uniform changes in appearance was noted for both artificially and naturally weathered samples according to the method recommended by ISO 4628 [36]. The coated panels were periodically rated for blistering, rusting and cracking according to ISO 4628 (Part 2, 3, 4) [37-39]. Degrees of flaking and filiform corrosion were assessed after the complete deterioration of coatings according to standard ISO 4628 (part 5, 10) [40-41].



Fig. 10: General view of the natural exposure test site.

Photographs of the test panels were taken, before and after exposure, with the purpose of determining the changes experienced by coatings. Scribed region was focused in the photographs because significant changes were observed in this region.

#### *Gloss Measurement*

Gloss of control and tested panels was measured according to the standard ISO 2813 [42]. Horiba IG-330 Gloss meter was used for this purpose. The samples were cleaned and 60° gloss was measured. Each sample was rotated about 45° after each measurement. A total of 10 measurements were made on each sample at each inspection. The data presented are the average of the measurements.

#### *Assessment of Degree of Corrosion Around the Scribe*

For the measurement of degree of corrosion, test panels were washed with fresh tap water and then dried in air. In order to expose the scribed region, coatings were removed with the help of paint

remover. After the removal of coatings, test panels were again washed with fresh tap water and then dried in air. This was followed by the application of varnish on the test panels (ISO4628-8) [43].

The degree of corrosion ( $c$ ) was calculated in millimeters for both artificially and naturally weathered samples, using the equation:

$$c = w_c - w/2$$

where:

$w_c$  is the mean overall width of the zone of corrosion, in millimeters;

$w$  is the width of the original scribe, in millimeters.

#### *Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analysis*

Scanning electron microscopy (SEM) was used to study the surface characteristics of control (unexposed) and exposed coating systems. Small sections of the coatings were coated with gold up to  $300\text{\AA}$  using a gold coater (JEOL JFC 1500). Finally the SEM micrograph was taken by using a Scanning electron microscope (JEOL 6380A), equipped with an X-ray detector for energy dispersive X-ray (EDX) analysis. The microscope was operated at  $10^{-7}$  Torr vacuum and 30 kV.

#### *Statistical Analysis*

Principal component analysis (PCA) was applied on the data obtained from EDX analysis in order to study correlation between accelerated and natural exposure testing. The data was processed by using the software Statistica (Version 10). The results were presented on a bi-dimensional plot and the significant loadings were marked when  $\geq |0.7|$ . PCA is a method of statistics used to trim down the dimensionality of a data set which contains a number of interrelated variables by maintaining the variation present in the data set.

#### **Conclusions**

In most cases, it is assumed that a 100 hours of exposure in salt spray by ASTM B-117 corresponds to about 1 year in the outdoors (Though no one says it with any degree of certainty, neither the coating manufacturer, nor the equipment manufacturers or the coating buyers). Many automotive industries specify 1400 hours of salt spray test for the ED primers by ASTM B-117 in a fond hope that the coating would last about 12-14

years, about the useful life of an automobile. The accelerated corrosion testing completely failed to correlate these norms with the results of natural exposure in marine environment of Karachi, Pakistan where several other factors appear to be causing much more accelerated corrosion. Following observations are note worthy.

1. The accelerated corrosion testing showed much less severity of corrosion compared to natural exposure testing for all the three coatings tested. This is most likely due to the presence of several corrosive components of environment emerging from the mist of salt spray in the atmosphere and pollution due to industry and automobiles. Air, as seen from the environmental data, contains large concentration of particulates; nitrous oxide sulfur compounds and sea salt are the most detrimental.
2. The loss of gloss was much higher in natural exposure testing for all the coatings tested.
3. Severe filiform corrosion was noticed in natural exposure testing compared to accelerated testing. This may be due to diffusion of corrosive salt /salts solution from the edges of the damage that were not present in the mist of accelerated salt spray test.
4. Spread of corrosion was far more severe in natural exposure testing.
5. Blistering was severe in natural exposure testing.
6. Surfaces of all the unexposed coating systems were smooth and featureless.
7. SEM micrographs suggested that the accelerated (salt spray) testing did not show surface features similar to those noticed after natural exposure testing. Accelerated (salt spray) testing revealed less degradation of the coating surface characteristics. In contrast, natural exposure testing caused drastic degradation of the coating surface characteristics.
8. Application of the Principal component analysis (PCA) on EDX data sets explained a variance of 99.98 %, 99.97 % and 99.29 % for  $P_1$ ,  $P_2$  and  $P_3$  coating systems respectively. These results clearly indicate that no correlation exists between accelerated test method ASTM B117 and natural exposure testing carried out at coastal industrialized location.

Based on the above observations, it is felt there is a need to devise a more stringent test protocol for coastal, industrialized locations than ASTM B 117 and it should be used for specifying the coatings for automotive paints. Some of the suggested changes are inclusion of highly corrosive bromide, sulfite and nitrate ions in acidic pH (6 to 6.5 or lower caused by acid rains) of the salt solution. In absence of such test methods, the

unsuspecting manufacturers of coating products and buyers of coating products are likely to suffer unexpected damage to their products. We propose to take up this work in collaboration with other researchers located in coastal industrialized locations of the world.

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