

Corrosion Resistance Synergistic Performance of Alkyd Based Triplex Coating System Impregnated with Fe, Zn, Cr and Ti based Corrosion Inhibitors

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Abstract: An alkyd polymer based triplex coating system embedded with Iron Oxide, Zinc Chromate and Titanium Dioxide inhibitors was studied to ascertain its corrosion resistance synergistic performance at various anthropogenic and metropolitan sites of Karachi coastal city while accelerated salt spray test was also carried out for reference. Coating performance was ascertained by visual morphological inspection, gloss measurements, Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray (EDX) analysis and by Fourier Transform Infrared (FTIR) Spectroscopy. EDX results substantiated a general increment in oxygen/carbon ratio and revealed that chromium was conspicuously vanished in all exposed coating systems. Diminution trend in gloss value, ex-corporation of inhibitors on the coating surface plus depletion of morphological features witnessed through SEM micrographs and curtailment of ester linkage signals in FTIR spectrum, concluded that an insignificant protection offered by the alkyd triplex coating due to its permeability upon weathering which led to ex-capsulation of inhibitors under moist conditions. Appraisal of these results have furnished an average coating performance correlation of 704 hpy (hours of salt spray test equivalence per year exposure test) at marine test site and 614 hpy at industrial test site in terms of blistering while equivalence mean in terms of rusting were found 815 hpy and 622 hpy at marine and industrial test sites respectively.

Key Words: Alkyd coatings, Corrosion inhibitors, Corrosion resistance, Galvanized steel.

Introduction

Polymeric coatings are effective mode of corrosion mitigation in structural materials. These coatings preserve underlying metals by virtue of their barrier effect, inductive (galvanic) effect and inhibition effect. Various additives are incorporated in coating formulation to introduce or boost these effects. Coatings can be classified on basis of these protection parameters as: singlet coatings have only barrier effect while duplex coatings have barrier plus inductive effects and triplex coatings have barrier, inductive and inhibition features [1-4]. A right coating formulation required best combination of these attributes for synchronized function and should be compatible to the service conditions. Synergistic interactions of these parameters are so complex with environmental variables that performance of a coating formulation did not remain predictable. A viable way out to this discrepancy is to design coating formulation as per service conditions requirement and ascertain its performance in real operational environment [5-8].

Alkyd is a class of coatings which chemically are polyesters modified with fatty acids. They are usually produced by a reaction between oils or fatty acids, polyols and dibasic acids or

anhydrides. Alkyd coating offers benefits of good adhesion, rapid drying, good flexibility, strength and durability at nominal cost; however alkyds cannot endure alkaline conditions [9, 10]. Being one-component air curing paints, alkyds coatings are feasibly applicable to substrate. They rendered freedom of formulation into both solvent-borne and water-borne coatings [11, 12]. In literature, various researchers have investigated the corrosion resistance of alkyd based coating systems [13-23].

Authors have previously reported results about performance attributes of various coating formulations, applied on mild steel and galvanized mild steel substrates [24-28]. In subject study, a triplex coating system was prepared by galvanizing a mild steel substrate and then by setting an alkyd primer embedded with iron oxide & zinc chromate inhibitors while alkyd topcoat loaded with titanium dioxide & iron oxide inhibitors was applied. In this communication, authors are reporting findings about corrosion resistance synergistic performance of alkyd triplex coating system, subject to various natural stimulating conditions (urban, marine, industrial) and artificial accelerated conditions (salt spray test).

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Experimental

Test Materials and Specimen Preparation

Electrogalvanized mild steel (EGMS) test coupons of dimensions 4" × 6" × 1.4 mm were first sand blasted and washed with solvent according to protocol SSPC-SP1 to remove grease and oils [29]. Then etch primer was mounted on each coupon. An alkyd primer embedded with Iron Oxide & Zinc Chromate inhibitors and an alkyd topcoat loaded with Titanium Dioxide & Iron Oxide inhibitors, were applied with an air-operated spray in compliance with the manufacturer's recommendations. This was followed by the drying of coated panels in air. The average dry film thickness of coating system (Primer + top coat) was measured with the help of Elcometer 456 digital coating thickness gauge and it was found to be 195 μm. Alkyd primer embedded with Iron Oxide & Zinc Chromate inhibitors and Alkyd top coat loaded with Titanium Dioxide & Iron Oxide corrosion inhibitors were procured from market. According to available information about its preparation; pigment stabilized emulsions were prepared. These pigments were then encapsulated by core-polymerization and transferred to the alkyd-resin. The pigment volume concentration (PVC) in the primer was 50 % while in the top coat it was 20 %. Surface of each dried and cured coated panel was scribed with an X, reaching the EGMS base in order to test coating resistance to the under film corrosion. Backsides and edges of specimens were secured with 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 as per ASTM B-117 norms. Salt spray chamber was used to provide high humidity (95-98 %) and continuous salt spray (5 % wt. NaCl) at 35 °C. Duly coated test coupons were affixed and orientated at 45° to the normal on plastic racks [30].

Natural Exposure Testing (NET)

NET was performed at three different anthropogenic and metropolitan test sites located in Karachi, Pakistan. NET was carried out according to ISO standard 8565 [31]. One set of prepared coated panels was placed at the marine exposure test site in Karachi, Pakistan. This test site was located at Hawke's bay of Arabian Sea coast (24° 51' 02.63" N, 66° 53' 08.26" E). Second set of coated panels was exposed at the industrial S.I.T.E area of Karachi, Pakistan (24° 54' 12.08" N, 67° 00' 34.21" E). Third

set was positioned for natural exposure at the urban test site (University of Karachi) in Karachi, Pakistan (24° 56' 40.37" N, 67° 00' 34.21" E). At the test sites, the test specimens (coated panels) were mounted on exposure rack, facing 45° southward.

Assessment of the Performance of Coatings

Performance of coating is rationally related with number of paint defects. During the visual inspection of the degradation of the coatings in the scribed region, coated panels were periodically rated for blistering, rusting and cracking according to ISO 4628 (Part 2, 3, 4) [32]. Degrees of filiform corrosion were assessed after the complete deterioration of coatings according to standard ISO 4628 (Part 10) [32]. Pre and post exposure test conditions of test panels were snapped in photographs to determine the deterioration experienced by coatings. Scribed region was focused in the photographs because significant changes may be observed in this region.

Gloss Measurement

Gloss of control and tested coupons were measured by Horiba IG-330 Gloss meter according to the ISO 2813 standard [33]. The samples were cleaned and 60° gloss was measured. Each sample was rotated about 45° after each measurement. A total of 10 readings were made on each sample at each measurement. Data reported were the average of the readings.

Assessment of Degree of Corrosion around the Scribe

Test panels were washed with fresh tap water and air dried. Coatings were removed with the help of paint remover to expose the scribed region. 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) [34]. Degree of corrosion around the scribe was visually ascertained.

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

Energy Dispersive X-ray analysis was carried out with an X-ray machine (JEOL 6380B) by employing Cu-K radiation. Small slices of coatings were cut from test coupons and EDX spectra were obtained by direct radiation on the specimen surface. Scanning electron microscopy (SEM) was also 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 A° using a gold coater (JEOL JFC 1500). Finally the SEM micrograph was taken by using a scanning electron microscope (JEOL 6380A), operated at 10⁻⁷ Torr vacuum and 30 kV.

Fourier Transform Infrared (FTIR) Spectroscopy

Chemical changes in the alkyd triplex coating exposed in natural outdoor and accelerated environments were investigated by Fourier transform infrared spectroscopy (FTIR). Infrared spectra were also taken for unexposed (control) coating systems. The whole coating systems including topcoat and primer were scraped from both the unexposed and exposed test panels and KBr discs were made. For exposed panels, it was ensured that the corrosion products were not included in the material used for testing. The spectra were obtained using a Shimadzu 8900 Fourier transform infrared spectrophotometer running with Omnic software, in the 4000-400 cm⁻¹ range. The spectrophotometer was operated in transmission mode. Spectra were recorded at a resolution of 2 cm⁻¹ and 20 scans.

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 $\geq |0.7|$.

Results and Discussion

Electrogalvanized mild steel (EGMS) test coupons (4" × 6" dimensions) painted by Etch/Alkyd Primer and Alkyd Topcoat System with various encapsulated corrosion inhibitors were subjected to atmospheric exposure of marine site (L₁), industrial site (L₂) and urban site (L₃), and also to accelerated (salt spray) testing. Details of procedures, positions and conditions were narrated in experimental section.

Coating performance was evaluated by visual inspection, gloss measurement, degree of corrosion around the scribe, Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) analysis and by Fourier Transform Infrared (FTIR) spectroscopy. Principal component analysis (PCA) was also carried out for the data obtained from EDX analysis in order to study correlation between accelerated and natural exposure testing.

Visual Inspection

Visual assessment of the morphological conditions of subject triplex coating systems was performed according to ISO norms 4628-1(Part 1) [32]. The standardized methods for the visual assessment of the performance of coatings are widely employed by the researchers [34, 35]. Assessment of degree of blistering, rusting and cracking was done according to standard ISO 4628 (Part 2, 3, 4) [32] from time to time while the degree of filiform corrosion was assessed by ISO 4628 (Part 10) [32] at the end of exposure. In these methods, the samples to be evaluated are compared to a set of standard photographs showing various degrees of each type of failure. For the assessment of blistering, the pictures in the ISO standard represent blister densities from 2 to 5, with 5 being the highest density. Blister size is also numbered from 2 to 5, with 5 indicating the largest blister. Results are reported as blister density followed by blister size. The scale used by ISO in assigning the degree of rusting ranges from Ri0 to Ri5, with Ri5 indicating the highest degree of rusting. The ISO method judge the degree of cracking in terms of quantity, size and depth together with approximate direction.

Scribes were engraved on alkyd cured EGMS test coupons to appraise coating performance when coating defects may be appeared due to mechanical impact (Fig 1). Visual assessment results were tabulated in Table-1 and 2.

Table-1: Results of visual examination of the anticorrosive performance of alkyd triplex coating system applied on electrogalvanized mild steel and exposed at different natural exposure test sites.

Test Sites	Coatings defects after																	
	12 months (May2006-May2007)			18 months (May2006-Nov2007)			21 months (May2006-Feb2008)			24 months (May2006-May2008)			27 months (May2006-Aug2008)			28 months (May2006-Sep2008)		
	B	R	Cr															
L ₁	0	0	0	2S ₃	2	0	4S ₃	4	0	5S ₃	5	0	d	d	d	d	d	d
L ₂	0	0	0	2S ₃	1	0	3S ₃	2	0	4S ₃	3	0	5S ₃	4	0	d	d	d
L ₃	0	0	0	0	0	0	0	0	0	2S ₂	1	0	3S ₂	2	0	d	d	d

L₁: Marine test site, L₂: Industrial test site and L₃: Urban test site,

B: blistering, R: rusting, Cr: Cracking, 0: No detectable paint defect, d: Panels were removed after exposure

Table-2: Visual examination results of accelerated (salt spray) testing of alkyd triplex coating system applied on electrogalvanized mild steel.

Coating defects	Time duration in hours			
	480	720	850	930
Blistering	0	0	2S ₂	3S ₂
Rusting	0	0	1	4

0 = No detectable paint defect

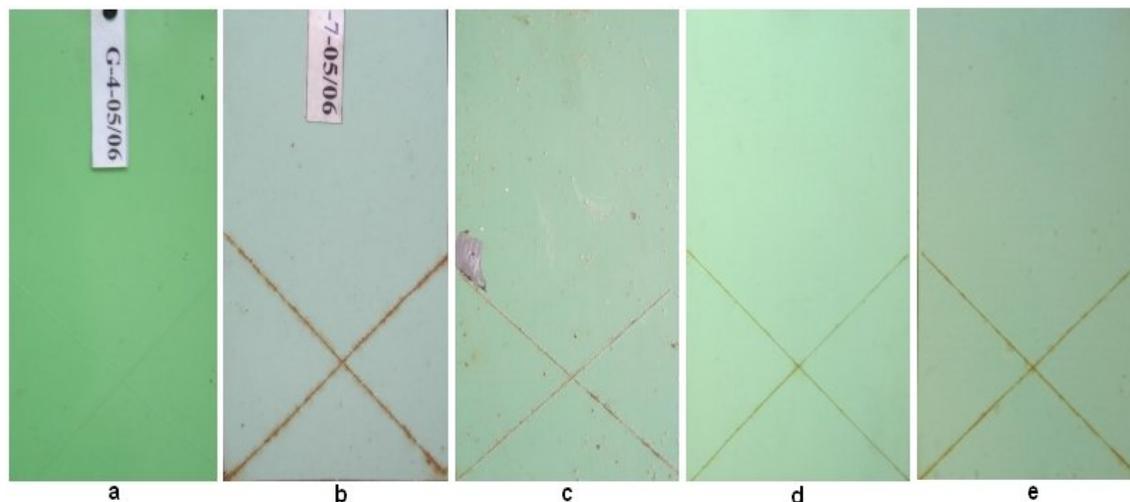


Fig. 1: State of scribed region of alkyd triplex coating systems over electrogalvanized mild steel (a) unexposed (b) after natural exposure testing at marine test site (c) after natural exposure testing at industrial test site (d) after natural exposure testing at urban test site (e) after accelerated (salt spray) testing.

Table-3: Correlation of alkyd triplex coating system performance at various natural exposure test sites and accelerated (salt spray) testing in terms of required time period for defects to be appeared.

Coating Defects	Blistering				Rusting				
	2S _x	3S _x	4S _x	5S _x	1	2	3	4	5
L ₁	18 months	20 months	21 months	24 months	15 months	18 months	20 months	21 months	24 months
L ₂	18 months	21 months	24 months	27 months	18 months	21 months	24 months	27 months	NA
L ₃	24 months	27 months	NA	NA	24 months	27 months	NA	NA	NA
SST	850 hrs	930 hrs	NA	NA	850 hrs	880 hrs	905 hrs	930 hrs	NA
Correl. SST/L ₁	567 hpy	558 hpy	-	-	680 hpy	587 hpy	543 hpy	531 hpy	-
Correl. SST/L ₂	567 hpy	531 hpy	-	-	567 hpy	503 hpy	453 hpy	413 hpy	-
Correl. SST/L ₃	425 hpy	413 hpy	-	-	425 hpy	391 hpy	-	-	-

L₁: Marine test site, L₂: Industrial test site, L₃: Urban test site, SST: Salt Spray Test

NA: Not achieved that defect level,

hpy: hours of SST equivalence per year of Natural exposure test

Natural exposure testing (NET) at marine site (L₁) indicated the formation of blisters and rust after 18 months of exposure. Increase in degree of blistering and rusting was noticed with respect to exposure time period while no cracking and filiform corrosion was witnessed. Further exposure was stopped after 24 months. Blistering and rusting were commenced after 18 months of NET at industrial site (L₂). With the passage of exposure time period; gradual increase in degree of blistering and rusting were experienced while cracking and filiform corrosion were not detected during exposure time period. Exposure test was winded up after 27 months of study (Table-1). NET at urban site (L₃) showed no signs of degradation even after 21 months of exposure however some blistering and rusting were observed after 24 months time span. Further study

was ceased after 27 months of exposure experiment (Table-1).

Main results of accelerated (salt spray) testing of the subject alkyd coating system were summarized in Table-2. There was no sign of degradation detected even after 720 hours of exposure. Some blisters and rust formation was commenced to appear after 850 hours which developed along with exposure time period. Further exposure experiment was terminated after 930 hours.

Aforementioned results categorically demonstrated the absence of any cracks or filiform corrosion around the scribe in alkyd triplex coating system even after 24 months of exposure to all above test sites. However, at marine test sites symptoms of

degradation and filiform corrosion were detected after 27 months exposure, indicating severity of marine environment.

Comparison of these results have furnished an average correlation in terms of blistering up to 562 hpy (hours of salt spray test equivalence per year exposure test) at L₁, 549 hpy at L₂ and 419 hpy at L₃ while equivalence mean in terms of rusting were found 585 hpy, 484 hpy and 408 hpy at L₁, L₂ and L₃ respectively (Table-3).

Gloss Measurement

Any topographical variation in coating surface may also be emulated in its gloss value therefore condition of coating could be rationally examined by monitoring gloss value of surface. Comparison of the gloss value of alkyd triplex coating systems measured under different exposures conditions were displayed in Fig 2. It was noticed after natural exposure testing that maximum reduction in gloss was recorded for the alkyd triplex coating system exposed at marine test site while minimum decrement in gloss was measured at urban test site. Comparison of the gloss measurements after accelerated (salt spray) and natural exposure testing revealed that the former induced less reduction in gloss of the coating system. Literature showed that B. del Amo, *et al.* studied the performance of alkyd paint containing zinc molybdenum phosphate corrosion inhibitors [34]. They ascertained the performance of alkyd paint through visual examination as per ASTM norms and by electrochemical and accelerated tests including salt spray test. E. Almeida, *et al.* reported the performance of alkyd paint on different substrates after various accelerated and natural exposure tests [35]. F. X. Perrin, *et al.* studied the degradation of alkyd topcoat [36] by different artificial weathering tests as well as by field tests at different locations. All abovementioned research work have studied diminution in gloss value of alkyd coating upon weathering and linked up this with loss of cross linking among organic materials of the coating.

It was apparent from the results obtained in this study that the natural exposure testing (particularly at marine and industrial test sites) caused high degradation of the coating systems tested as compared to accelerated testing. It was assumed that modes of degradation may be similar on account

of key factor of 'salt spray' playing role both in natural weathering in form of mist of salt spray emerging in the atmosphere and also in accelerated (salt spray) test. However, it was found completely different in accelerated and natural exposure testing. That was most likely due to the presence of several corrosive constituents of marine and industrial environment, emerging from the mist of salt spray in the atmosphere and due to industry and automobiles pollution which caused high degradation of the binder and loss of cross linking hence small organic units formed and eliminated from the polymer matrix while on other hand these factors were absent in the mist of accelerated salt spray test.

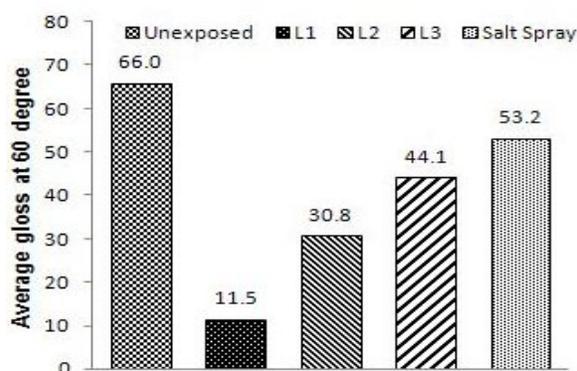


Fig. 2: Comparison of the gloss value of alkyd triplex coating systems subject to unexposed testing, natural exposure testing at marine test site (L₁) industrial test site (L₂) urban test site (L₃) and accelerated (salt spray) testing.

Scanning Electron Microscopy (SEM) Analysis

Customarily, a coating film protects underlying metal substrate by cordoning off its contact with environmental corrodants. Prolong weathering caused polymeric degradation of coatings vide photo-oxidation processes which reduces barrier function of coating by producing cracks in surface morphology. SEM is a powerful technique to take a high resolution sight of surface topography therefore helpful to monitor the variations in the superficial properties of coatings due to weathering [37]. In subject study, SEM was also employed to record topographic micrographs of test panels after their exposure to various natural and accelerated environments (Fig. 3).

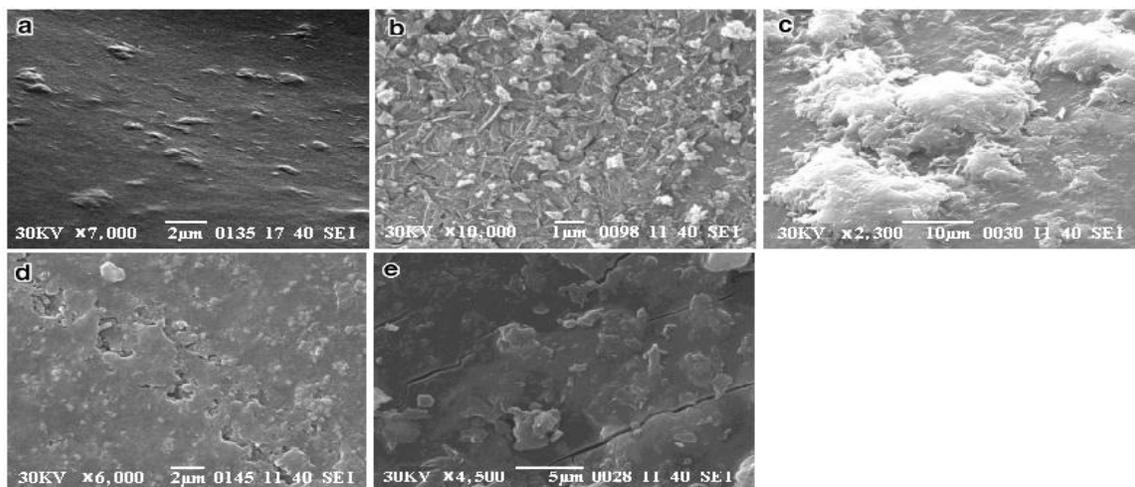


Fig. 3: Scanning electron micrographs of the surface of alkyd triplex coating systems applied on electrogalvanized mild steel (a) unexposed (b) after natural exposure testing at marine test site (c) after natural exposure testing at industrial test site (d) after natural exposure testing at urban test site (e) after accelerated (salt spray) testing.

In SEM micrographs, surface of the unexposed alkyd triplex coating system was appeared smooth and featureless (Fig 3a) while NET at marine site (L_1) has exhibited severely roughened coating's surface with large size cracks (Fig 3b). SEM micrographs of NET at industrial site (L_2) illustrated destroyed surface with significant cracks on surface (Fig 3c) while NET at urban site (L_3) indicated irregular degradation of the coating surface characteristics without any cracks (Fig 3d). Similarly accelerated (salt spray) test showed considerable changes in the coating's surface characteristics in the form of surface roughening and cracks (Fig 3e). Examination of the surface morphology of the alkyd triplex system by SEM after NET revealed that the degradation of the binder resulted in irregular surface and erosion of pigments on the surface.

SEM technique was opted by several scientists to investigate the effects of weathering on alkyd coatings [38, 39]. B. S. Skerry, *et al.* reported a study in which they employed SEM to examine the changes occurred in alkyd coating after accelerated (salt spray) and natural exposure testing in industrial environment [40]. According to their study, SEM micrographs indicated severe degradation in the surface characteristics of alkyd coating as a result of natural exposure testing at industrial site as compared to accelerated (salt spray) testing. F. X. Perrin, *et al.* also carried out investigation by SEM and FTIR spectroscopy to study the defects produced in alkyd coating after accelerated and NET in marine and industrial environments [36]. Results obtained in their study also indicated severe degradation in the surface characteristics of alkyd coating as a result of

NET particularly at marine and industrial test sites. They revealed that the defects produced as a result of weathering could not be associated to the physico-chemical changes of the binder. Since they found that accelerated testing caused the less degradation of the surface of alkyd coatings as elucidated by SEM micrograph while contrary to this, FTIR spectroscopy indicated severe chemical changes. Results obtained in our study were also consistent with these findings.

Energy Dispersive X-ray (EDX) Analysis

Energy Dispersive X-ray (EDX) technique is a useful tool to analyze the elemental composition of weathering products deposited at coating surface by direct radiation on the aged surface of test panels. Fig 4 depicted the energy dispersive X-ray (EDX) spectra of alkyd triplex coating system surface after NET at different test sites as well as after accelerated (salt spray) testing while Table 4 presented its surface composition data as determined by EDX analysis. EDX analysis performed for the unexposed alkyd triplex coating system have indicated the presence of C, O, Na, Al, Si, S, Cl, Ca, Cr, Ti, Fe, Cu, Zn and Fe elements in peripheral layer (Fig 4a). NET at marine site (L_1) corroborated the occurrence of C, O, Mg, Al, Si, Cl, K, Ca, Ti, Fe and Zn (Fig 4b) whereas NET at industrial site (L_2) showed the presence of C, O, Na, Mg, Al, Si, Cl, Ca, Ti and Fe with different % abundance (Fig 4c). Natural exposure testing at urban site (L_3) illustrated the presence of C, O, Al, Si, Cl, Ca, Ti, Fe, Cu, and Zn (Fig 4d) while C, O, Na, Al, Si, Cl, Ca, Ti, Fe, Cu, and Zn were found after accelerated (salt spray) testing (Fig 4e). Comparison of elemental composition of unexposed and exposed

coating system revealed that chromium was conspicuously absent in the all exposed coating systems. Chromium may be washed out by dew precipitation on coating surface during early dawn due to its high water solubility. Moreover, Zn was surprisingly found absent in EDX results of coated panels exposed to industrial environment. This may be due to fact that diminution trend in gloss values, EDX analysis, FTIR spectroscopy and SEM micrographs, all revealed high degradation in the

surface characteristics of coating during natural exposure testing at industrial test sites. Which may be due to presence of several corrosive pollutants in industrial exhaust that caused high degradation of the binder and loss of cross linking hence small organic units formed and eliminated from the polymer matrix? All this resulted, in ejection of inhibitors. This is also evident from high erosion of pigments on the surface in SEM image of industrial exposed coated panel.

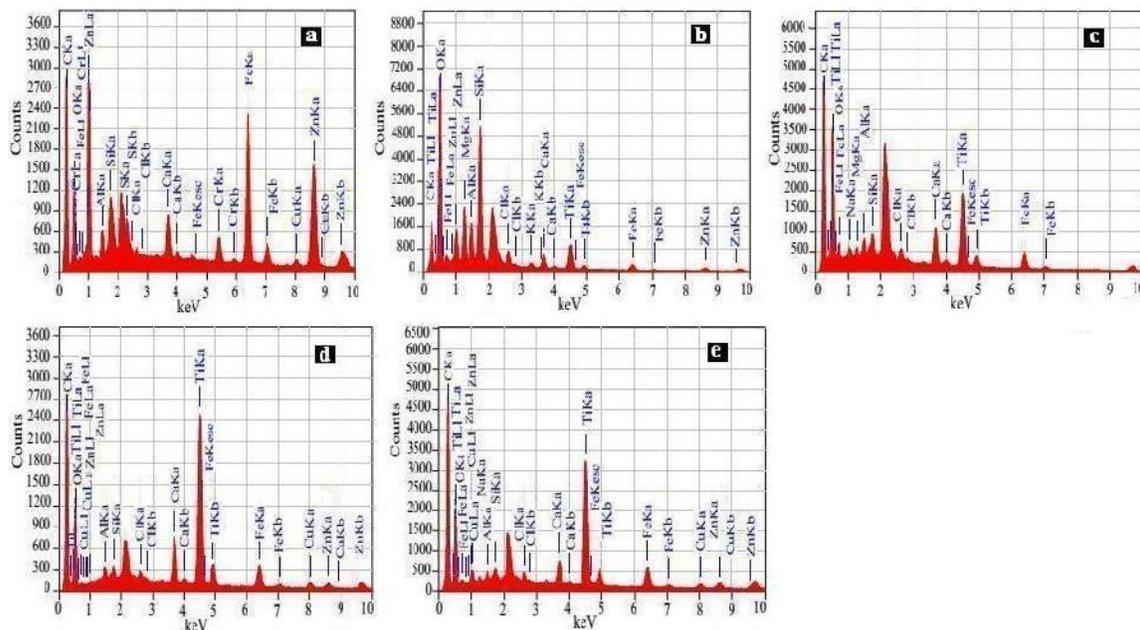


Fig. 4: EDX spectra of the surface of alkyd triplex coating systems applied on electrogalvanized mild steel (a) unexposed (b) after natural exposure testing at marine test site (c) after natural exposure testing at industrial test site (d) after natural exposure testing at urban test site (e) after accelerated (salt spray) testing.

Table-4: Surface composition data of alkyd triplex coating systems applied on electrogalvanized mild steel as determined by EDX analysis.

Element	Binding Energy	Unexposed	NET at L ₁	NET at L ₂	NET at L ₃	SST
	kev	mass%	mass%	mass%	mass%	mass%
C	0.277	49.42	18.59	33.09	44.75	47.54
O	0.525	21.76	46.55	38.44	39.29	38.71
Na	1.041	1.81	0	0.85	0	1.04
Mg	1.253	0	4.9	0.55	0	0
Al	1.486	1.06	2.67	0.92	0.58	0.44
Si	1.739	0.92	10.25	0.9	0.31	0.31
S	2.307	0.3	0	0	0	0
Cl	2.621	0.22	1.55	1.09	0.26	0.34
K	3.312	0	0.53	0	0	0
Ca	3.69	1.1	1.94	3.84	1.74	0.9
Cr	5.411	1.04	0	0	0	0
Ti	4.508	7.05	5.62	13.31	9.42	7.14
Fe	6.398	9.09	2.9	7.02	2.02	1.99
Cu	8.04	0.61	0	0	0.9	0.68
Zn	8.63	5.61	4.5	0	0.72	0.91
Total		100	100	100	100	100

NET : Natural Exposure Testing, SST : Salt Spray Testing,
L₁ : Marine test site, L₂ : Industrial test site, L₃ : Urban test site

Fig. 5 demonstrated the comparison of oxygen/carbon (O/C) ratios in unexposed and exposed alkyd triplex coating systems. Maximum O/C ratio was found after NET of alkyd triplex coating system at marine test site (L_1) followed by at industrial test site (L_2) and at urban test site (L_3) respectively. Comparison of O/C ratios obtained after accelerated (salt spray) testing with that obtained after NET at marine (L_1) and industrial (L_2) test sites revealed that O/C ratio was higher in latter cases. Increase in oxygen contents upon weathering was also noticed by some researchers. C. Pirvu, *et al.* has investigated the changes in the surface morphology of the alkyd coatings by using SEM along with EDX spectroscopy [39]. They also experienced an increase in oxygen and iron contents of the coating after degradation. They related this increase in contents to the development of rust beneath the paint film. In a study reported by X. F. Yang *et al.* [41], they suggested that the reaction of atmospheric oxygen and the formation of several oxidation photoproducts as a result of weathering is the main cause for increase in oxygen contents. C. Perez, *et al.* investigated in detail the performance of alkyd coating on galvanized steel and used SEM-EDX to interpret the performance of the duplex system. They concluded that the better protective properties were due to the formation of a zincite layer under the duplex system. However, the use of alkyd coating on galvanized substrate is not favored in marine environment because of the fact that in wet areas zinc can produce alkaline surface. Use of alkyd coating on an alkaline surface can cause saponification and in turn cause premature failure of the coating [42].

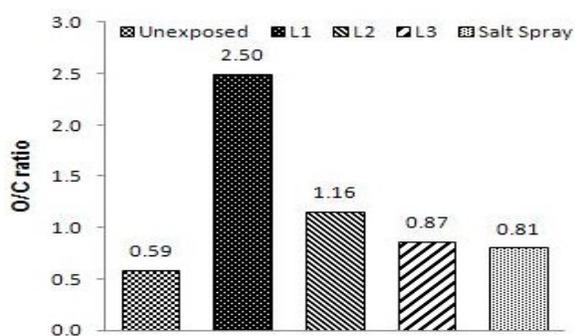


Fig. 5: Comparison of O/C ratios in alkyd triplex coating systems subject to unexposed testing, natural exposure testing at marine test site (L_1) industrial test site (L_2) urban test site (L_3) and accelerated (salt spray) testing.

Results obtained in our study for alkyd coatings were in good agreement with these findings in literature. An increase in oxygen content and O/C

ratio was noticed in subject study after accelerated and natural exposure testing. Whereas high values of O/C ratios obtained after NET at marine (L_1) and industrial site (L_2) as compared to artificial ageing may be attributed to photo-oxidative degradation of the binder in the former case and not in the latter case as ASTM B117 does not include an exposition to UV radiation. EDX results substantiated a general increment in O/C ratio after NET at all test sites as well as after accelerated (salt spray) testing. These increments showed an insignificant protection offered by the alkyd coating due to its permeability upon weathering which lead to corrosion.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectrometer is a valuable instrument to study chemical changes (degradation) in terms of functional groups that occurred in organic coatings while degree of these changes (degradation) is directly associated with intensity of FTIR signals [43]. Ester linkages are structural backbone of alkyd coatings [44]. FTIR spectrum of an unexposed alkyd triplex coating system (Fig. 6a) has shown ester carbonyl vibration as a strong, sharp band in the 1720-1740 cm^{-1} region. Peak observed in the range of 4000-3200 cm^{-1} was an indication of O-H stretching. Absorbance at 1280 cm^{-1} was associated with C-O stretching of ester moiety while C-O stretching of O-CH₂ moiety was observed at 1121 cm^{-1} . All these bands were characteristic of an alkyd resin [45, 46].

FTIR spectra obtained for alkyd triplex coating systems after NET at marine, industrial and urban test sites as well as after accelerated (salt spray) testing showed changes in the similar regions independent of type of exposure testing (Fig. 6). These changes included: Firstly, an important diminution of the signal for ester carbonyl vibration in the 1720-1740 cm^{-1} region which accounts for loss of ester linkages from polymeric backbone of alkyd and secondly, emergence of new peaks for carbonyl vibration in 1560-1628 cm^{-1} range which may be associated with formation of various photo-oxidized species such as carboxylic acids, aldehydes and ketones. These observations have indicated that photo-Fries intramolecular rearrangement or hydrolytic degradation were probably major mode of aging. Besides showing peaks in similar regions, comparison of the peak intensity indicated that after NET maximum degradation of the coating systems occurred in marine environment (Fig 6b) while less degradation of the coating systems was observed in urban environment (Fig 6d).

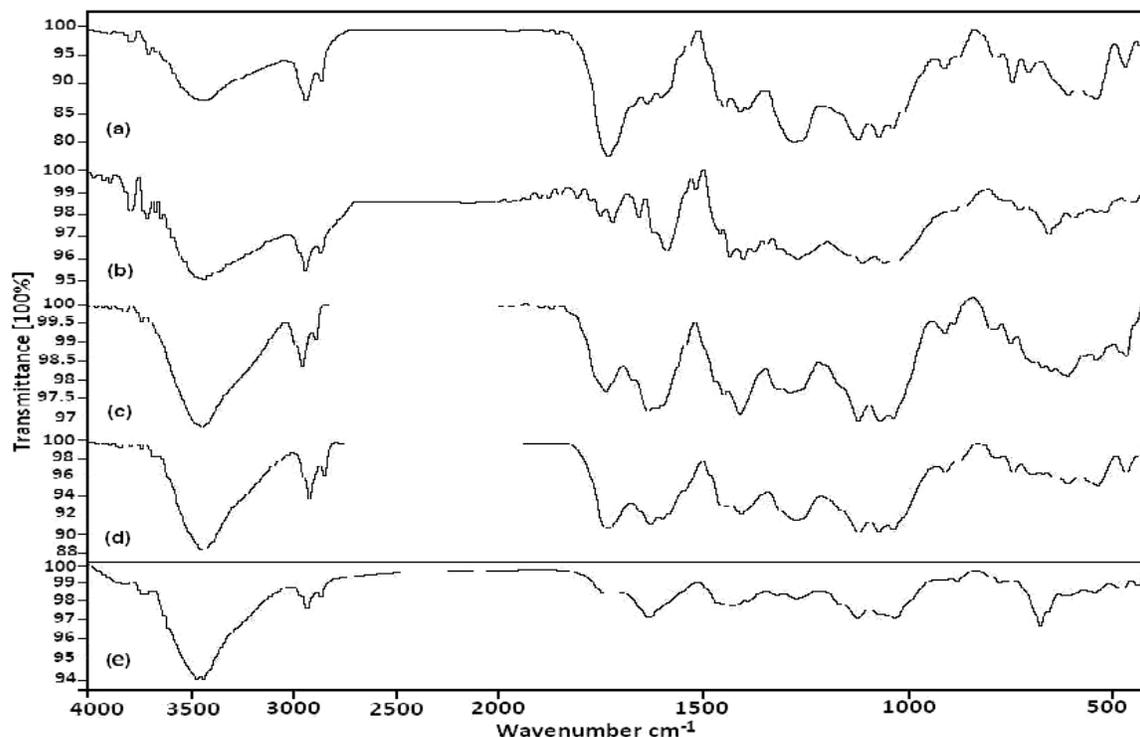


Fig. 6: Infrared spectra comparator of alkyd triplex coating systems applied on electrogalvanized mild steel (a) unexposed (b) after natural exposure testing at marine test site (c) after natural exposure testing at industrial test site (d) after natural exposure testing at urban test site (e) after accelerated (salt spray) testing.

Several researchers have investigated photodegradation of alkyd coating by FTIR. C. Ocampo, *et al.* used FTIR spectroscopy and compared the anticorrosive performance of unmodified and modified alkyd paints against marine corrosion [38]. F. X. Perrin, *et al.* reported the mechanism of photodegradation of alkyd coatings [36]. They observed that the major difference between unexposed and exposed alkyd coatings were in the regions of hydroxyl and carbonyl stretching around 3400 and 1720 cm^{-1} respectively. In another study reported by F. X. Perrin, *et al.* they studied the degradation of alkyd coating under different standard test conditions. They observed loss of ester linkages from the backbone of alkyd coating. They have proposed this depletion was due to photo-Fries intramolecular rearrangement or hydrolytic degradation. However, detailed study proved that the degradation of alkyd coating is mainly influenced by the hydrolytic processes while UV radiation did not affect the degradation of alkyd coating [47].

Comparison of FTIR results of subject alkyd triplex coating system applied on electrogalvanized mild steel substrates with our previous published study of alkyd singlet coating system at mild steel substrate, revealed high degradation upon NET in

former case [25]. This may be due to fact that zinc can produce alkaline surface in moist conditions. Alkyd coating contains ester framework of fatty acid thus can suffered with saponification which in turn cause decomposition of coating.

Principal Component Analysis

Data obtained from EDX analysis was statistically processed through Principal Component Analysis (PCA). This 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. The Principal component analysis of alkyd triplex coating systems with electrogalvanized mild steel substrate explained a variance of 98.3 % when 2 components were considered. The variance of the first component was explained by the negative and non-significant loadings of the Unexposed, NET at L_1 , NET at L_2 , NET at L_3 and SST which were not correlated each other. The variance of the second component was explained by the negative and non-significant loadings of the NET at L_1 and NET at L_2 , whereas the positive contributions were mainly due to Unexposed, NET at L_3 and SST (Fig. 7). However, these contributions were also not significant.

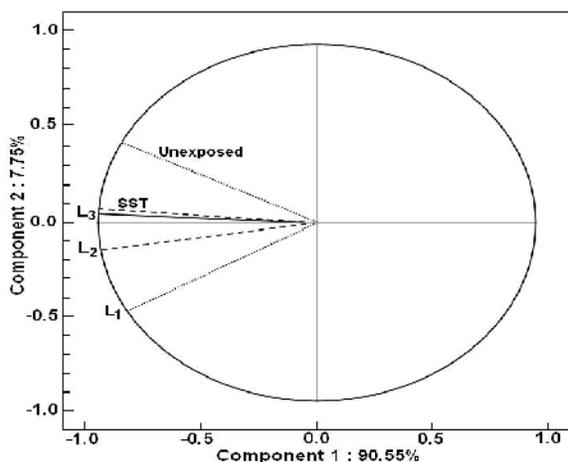


Fig. 7: Loading plots of the principal component analysis reported the results of the elaborations carried out with EDX data sets obtained for triplex alkyd coating systems (in the axis title of each component explained variance is reported).

Conclusions

This study corroborated the employment of chromate inhibitors unsuitable for moist conditions due to its high water solubility as EDX data of coating composition revealed that chromium was conspicuously absent in the all exposed coating systems which may be washed out by dew precipitation on coating surface during early dawn. This is also substantiated by SEM micrograph which depicted erosion of additives on the coating surface after exposure test. Whereas zinc compounds was also found inappropriate for hydrated environment as create alkaline conditions which are fatal for alkyd coatings as promote hydrolysis of ester linkage in alkyd polymeric backbone. These findings restrict the loading of zinc chromate as inhibitors in alkyd coating system for high humidity service conditions. FTIR signals diminution in the $1720-1740\text{ cm}^{-1}$ region account for loss of ester linkages from polymeric backbone of alkyd while emergence of new peaks for carbonyl vibration in $1560-1628\text{ cm}^{-1}$ range can be associated with the formation of various photo-oxidized species such as carboxylic acids, aldehydes and ketones. These FTIR results have indicated that photo-Fries intramolecular rearrangement or hydrolytic degradation were probably major mode of aging.

Aforementioned results in view, this study concluded that although subject alkyd triplex coating systems offered appropriate protection under dry conditions however, it did not perform good corrosion resistant synergistic function to avert

corrosion under moist conditions of marine. All three components of subject alkyd triplex coating system i.e. alkyd matrix, corrosion inhibition additives and galvanized layer found incompatible hence not worked synergistically in marine environment. Due to permeability of alkyd resin upon weathering, embedded corrosion inhibition additives decapsulated and washed out from coating system by splashing of droplets or by dew precipitation. Moreover, in moist environment galvanized layer produced alkaline conditions which deteriorated alkyd ester framework by hydrolytic cleavage.

Diminution trend in gloss values, EDX analysis, FTIR spectroscopy and SEM micrographs, all revealed high degradation in the surface characteristics during natural exposure testing (particularly at marine and industrial test sites) as compared to accelerated testing. This was more likely due to the presence of several corrosive pollutants in coastal environment, emerging from windblown spray droplets, marine fog and industrial & automobiles exhaust which caused high degradation of the binder and loss of cross linking hence small organic units formed and eliminated from the polymer matrix on the other hand these environmental detrimental factors were absent in accelerated test. Comparison of performance of subject alkyd triplex coating system applied on electrogalvanized mild steel substrates with our previous published study of alkyd singlet coating system at mild steel substrate revealed high degradation upon NET in former case [25]. This may be due to fact that zinc can produce alkaline surface in moist conditions. Alkyd coating contains ester framework of fatty acid thus can suffered with saponification which in turn caused decomposition of coating. Findings of subject study demand development of robust coatings for preservation of metallic structures at these corrosive natural environment sites. Therefore, our future research would be oriented towards exploration cum development of various robust coating systems compatible with marine conditions for preservation of mild steel and electrogalvanized mild steel structures. We have planned an extensive study for ascertaining shortcomings in currently employed coating systems responsible for underperformance. Based on these findings, various coating formulations would be worked out to develop new robust coating system compatible with severe corrosive conditions of Karachi coastal city.

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Declaration of interest

Authors declare that they have no conflict of interest.

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