EVALUATION OF ELECTROCHEMICAL AND STRUCTURAL PROPERTIES OF POLYURETHANE COATING ON STEEL SURFACES FOR CORROSION RESISTANCE

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AIM

- **Investigation of corrosion additives that can be alternatives to zinc phosphate in terms of corrosion resistance in polyurethane paints.**
- **Examined corrosion additives:**

  - Inhibisphere A

  - Inhibisphere ZS

  - Cerium octoate

POLYURETHANE

- Polyurethane (PU) is one of the largest polymer products in the plastic family.
- From a chemical perspective, the main components of PU are macro-diol (functional group: OH) and polyisocyanate (functional group: NCO).
- These two functional groups form extended chains and networks bonded by urethane link which is formed as a result of exothermic reaction.
- Polyurethane was patented by Otto Bayer in 1937.

POLYURETHANE TYPES AND APPLICATIONS

Table 1: Types and applications of polyurethane

POLYURETHANES

Thermoplastic PU	Flexible PU	Rigid PU	PUI (Polyurethane ionomers)	Water-borne PU
Examples: Keyboard protector for laptop, outer cases of mobile electronic devices, automotive instrument panels, caster wheels, power tools, sporting goods, medical devices, drive belts, footwear, inflatable rafts, and a variety of extruded film, sheet and profile applications	Examples: Cushion materials, carpet underlays, furniture, bedding, automotive interior parts, packaging, biomedicine and nanocomposites	Examples: Thermal and sound insulators	Examples: Artificial hearts, connector tubing for heart pacemakers and hemodialysis tubes	Examples: Adhesives, sealants, binders

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ChemMedia by Artkim Group

Akindoyo, J. O., Beg, M. D. H., Ghazali, S., Islam, M. R., Jeyaratnam, N. And Yuvaraj, A. R., 2016, Polyurethane Types, Synthesis And Applications-A Review, The Royal Society of Chemistry, 6:114453–114482p.

CORROSION MECHANISM AT STEEL SURFACES

- **Corrosion is the process that a material deterioration as a result of electrochemical and chemical reactions with its environment.**

- **It is an important problem that must be prevented as it can cause decoration failure, material losses and significant economic losses.**

CORROSION MECHANISM AT STEEL SURFACES

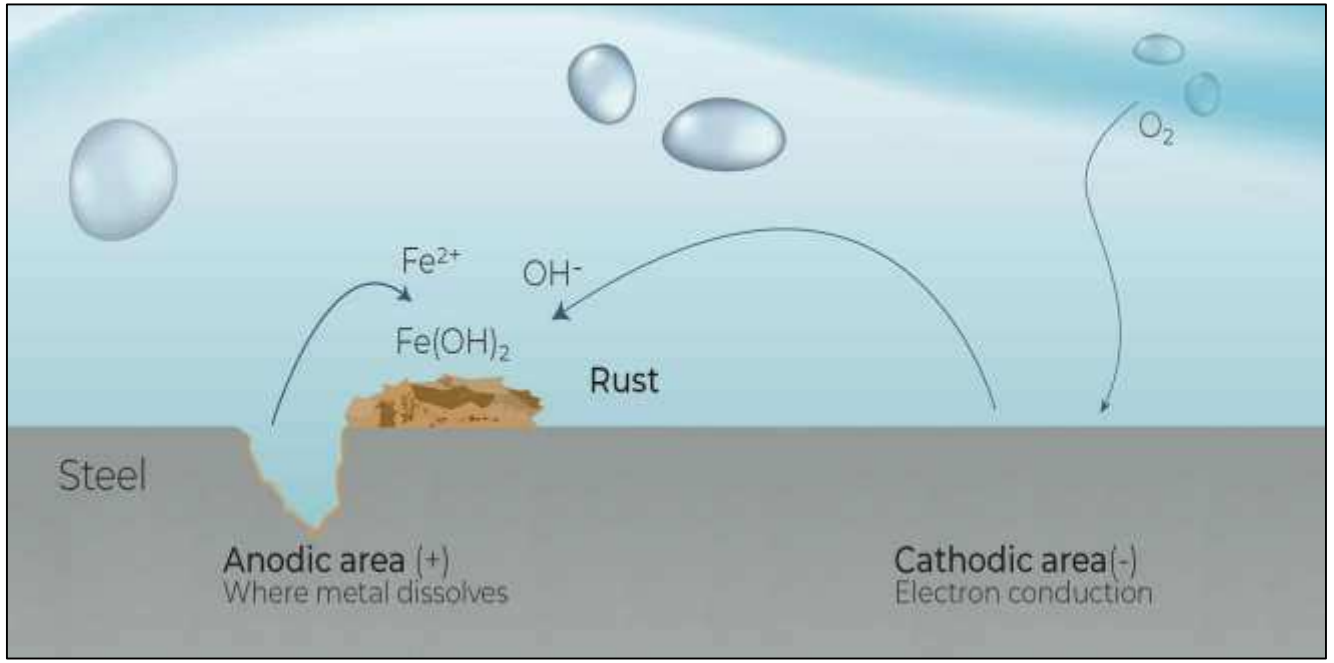


Figure 1: Corrosion mechanism of steel surfaces

$$4Fe+3O_2 \longrightarrow 2Fe_2O_3$$

Anodic reaction: $Fe \longrightarrow Fe^{+2} + 2e^-$

Cathodic reaction: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Buchheit, R.G., 2018, Handbook of Environmental Degradation of Materials (Third Edition), William Andrew Publications, United States, 449-468pp.

POLYURETHANE COATINGS

- **Coatings are one of the most important methods for metallic materials to protect against corrosion.**
- **Polyurethane coatings are considered to act as barriers by trying to prevent the passage of oxygen, water and ions between the surface and the environment.**

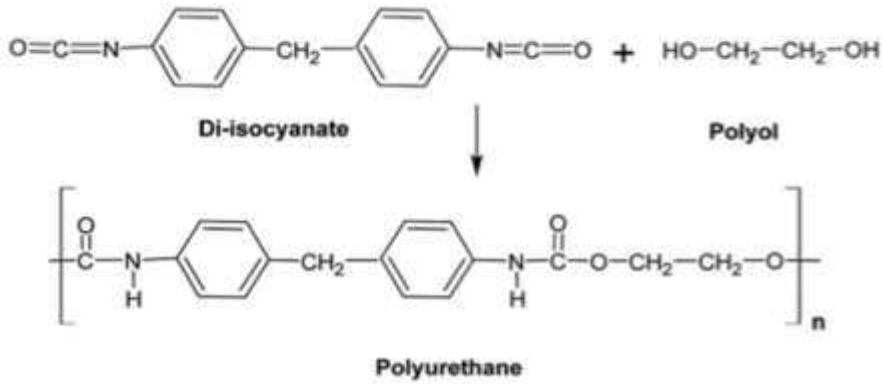


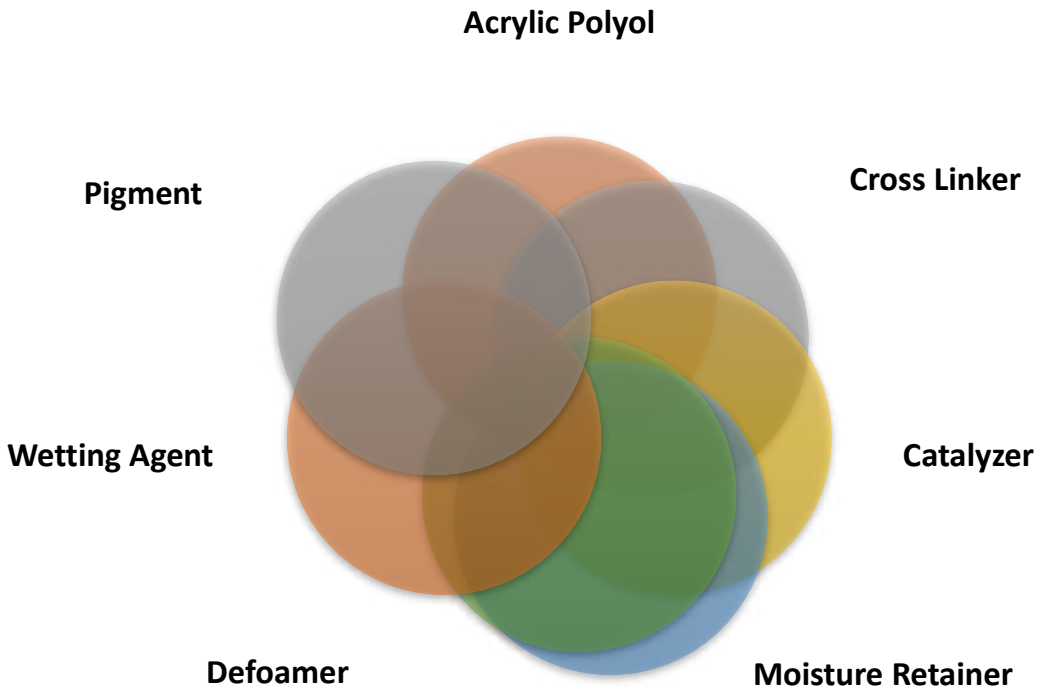
Figure 2: The synthesis reaction of a typical PU

Lyon, S.B., Bingham, R. and Mills, D.J., 2017, Advances in corrosion protection by organic coatings: what we know and what we would like to know, Progress in Organic Coatings, 102:2-7pp.

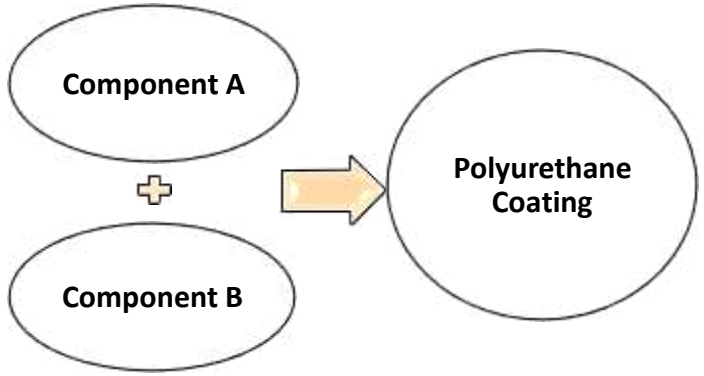
Gogoi, R., Alam, M.S. and Khandal, R.K., 2014, Effect of increasing NCO/OH molar ratio on the physicomechanical and thermal properties of isocyanate terminated polyurethane prepolymer, International Journal of Basic and Applied Sciences, 3(2):118-123pp.

CONTENTS OF POLYURETHANE COATING

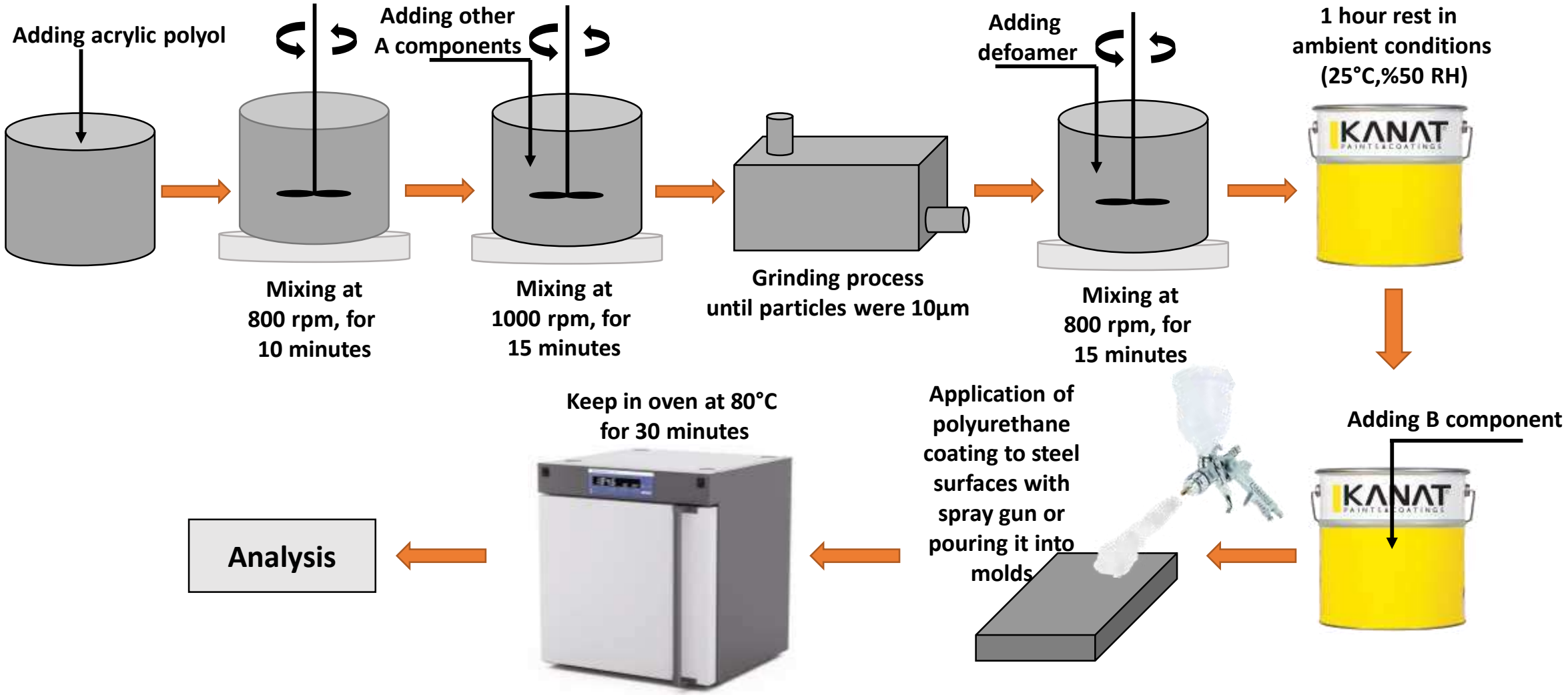
Component A of PU Coating



Component B of PU Coating



POLYURETHANE COATING PREPARATION



PREPARED POLYURETHANE COATING PROPERTIES

Table 2: Prepared polyurethane coating properties

NCO:OH RATIO	PVC VALUE (%)	DRY FILM THICKNESS OF POLYURETHANE COATINGS	ADDITIVES	PROPERTIES OF ADDITIVES	PARTICLESIZE (µ)	WEIGHT PERCENTAGE OF ADDITIVES (% wt)
1.1	35	50-60 µ	Zinc phosphate	$Zn_3(PO_4)_2$	2-3.5	1.88
			Inhibisphere-A	organosilica	0.3-0.6	1.88
			Inhibisphere-ZS	pure silica	20-40	1.89
			Cerium octoate	$C_{24}H_{45}CeO_6$ (liquid)	-	1.87
			No additive	Reference panel	-	-

ANALYSIS AND USED STANDARDS

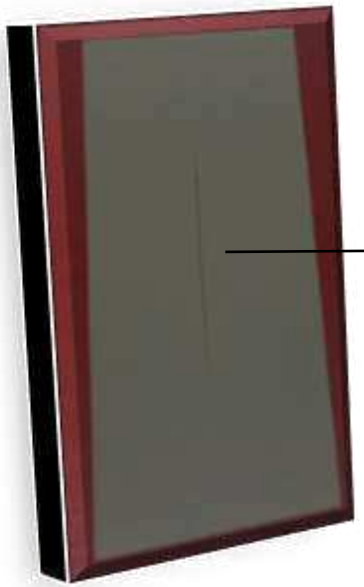
Polyurethane coatings analysis are in the table below.

Table 3: Analysis and used standards

ANALYSIS NAME	USED STANDARD	ANALYSIS TIME
Neutral Salt Spray Test	ISO 9227 NSS	For 21 Days
Electrochemical Impedance Spectroscopy Tests	Nyquist and Bode Plots, Linear Polarization Resistance and Potentiodynamic Polarization Resistance (Tafel)	For 0 and 21 Days
SEM Analysis	SEM/EDX	-
Hardness measurements	ISO 1522	-
Chemical Resistance Tests	AWWA C222	For 30 days

NEUTRAL SALT SPRAY TEST

- **Salt spray testing was carried out according to ISO 9277 NSS standard by exposing the coated panels to salt spray corrosion cabinet maintained at 35 ˚C, %100 RH and 0.82 bar pressure for 500 hours (concentration of salt solution: %5).**



Scribe with the length of 5-6 cm and 1 mm width

NEUTRAL SALT SPRAY TEST

Figure 3: Panel's photograps after 500 hours corrosion test

Table 4: Corrosion test results for 500 hours

Corrosion test time	Evaluation Standard	No additive	Containing zinc phosphate	Containing inhibisphere A	Containing inhibisphere ZS	Containing cerium octoate
		Dry film thickness: 50-60µ	Dry film thickness: 50-60µ	Dry film thickness: 50-60µ	Dry film thickness: 50-60µ	Dry film thickness: 50-60µ
500 hours	Blister (ISO 4628-2)	No 4 Few, No 6 Few	No 8 Few	No 8 Few	No 8 Dense	No 4 Medium, No 6 Few
	Surface rust (ISO 4628-3)	Ri 0	Ri 0	Ri 0	Ri 0	Ri 1
	Scribed line corrosion (mm) (ISO 4628-8)	6	5	3	9	6
	Delamination (mm) (ISO 4628-8)	7	4	4	15	6

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY TEST

- **Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the current through the cell.**

- **Impedance measurements were performed using 3 different techniques.**

- Nyquist and bode plots,
- Linear polarization resistance,
- Potentiodynamic polarization (Tafel).

Figure 4: The corrosion test cell

Tafel Curves (Potentiodynamic Polarization)

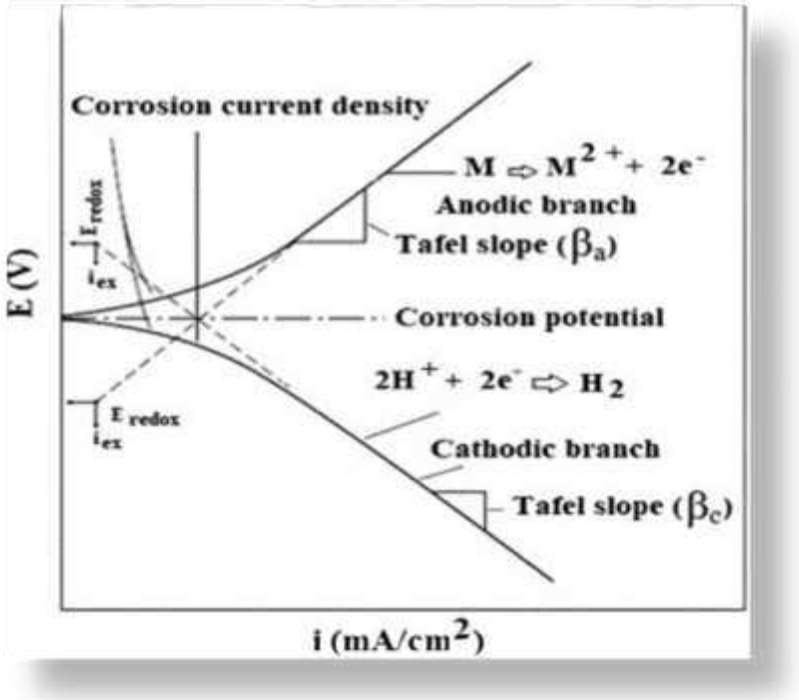


Figure 5 : Tafel curves

- In the Tafel extrapolation method, anodic and cathodic Tafel curves (branches) are obtained for the corroded metal.
- Extrapolation is performed by extending the linear portions of the anodic and cathodic plots back to their intersection.

Tafel Curves (Potentiodynamic Polarization)

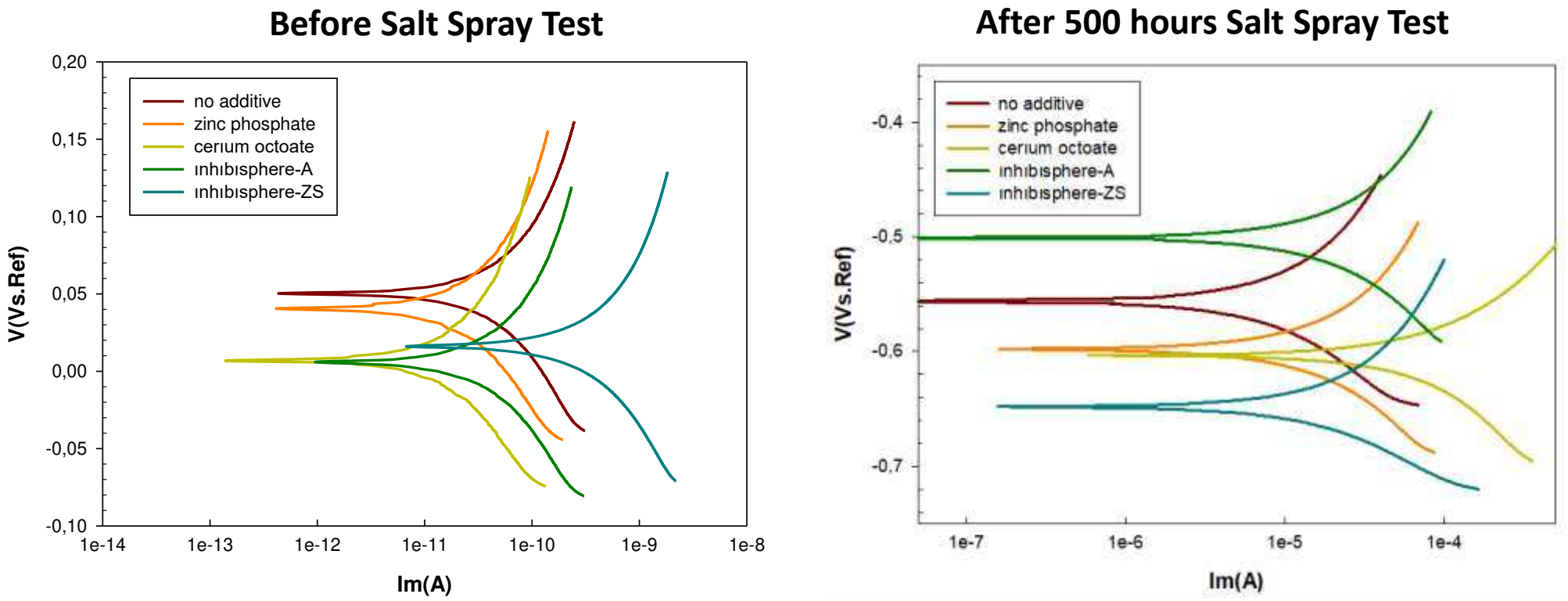


Figure 6: Tafel curves of different polyurethane coatings

Tafel Curves (Potentiodynamic Polarization)

Table 5 : Tafel curves of different polyurethane coatings before and after 500 hours salt spray test

Corrosion test time	Polyurethanes	Icorr	Corrosion Rate, mpy (mils per year penetration)	Polarizaion resistance (Rp)
Before corrosion test	No additive	278 pA	$7.97x10^{-6}$	322.4 Mohm
	With zinc phosphate	250 pA	$6.2\ x10^{-6}$	450.2 Mohm
	With ınhibisphere A	200 pA	$5.74\ x10^{-6}$	560.8 Mohm
	With ınhibisphere ZS	1490 pA	$47.76\ x10^{-6}$	50.08 Mohm
	With cerium octoate	61.60 pA	$1.76\ x10^{-6}$	912.4 Mohm
After 500 hours corrosion test	No additive	59.5 µA	2.199	1.160 kohms
	With zinc phosphate	52.10 µA	1.493	1.426 kohms
	With ınhibisphere A	35.2 µA	0.171	2.409 kohms
	With ınhibisphere ZS	57.30 µA	4.285	0.259 kohms
	With cerium octoate	146 µA	4.178	1.003 kohms

Linear Polarization Resistance Curves

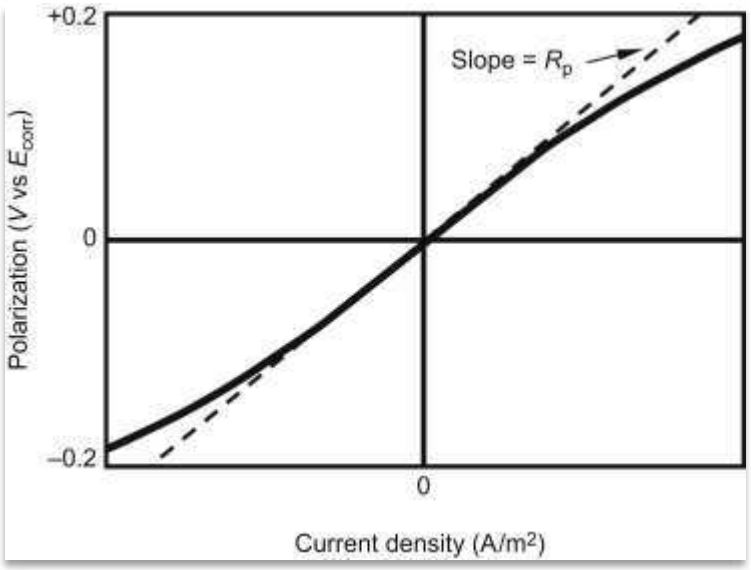


Figure 7 : LPR curves

- A linear polarization resistance (LPR) test is a corrosion rate monitoring method and it can give an indication of the corrosion resistance of materials in an aqueous environment.
- Rp reflected the coating's ability to block electrolyte penetration; the larger the Rp, the stronger the coating system's blocking effect on corrosion ions.

Linear Polarization Resistance Curves

Table 6: Polarization resistance (Rp) and corrosion rate (CR, mpy) of different polyurethanes before and after 500 hours salt spray test

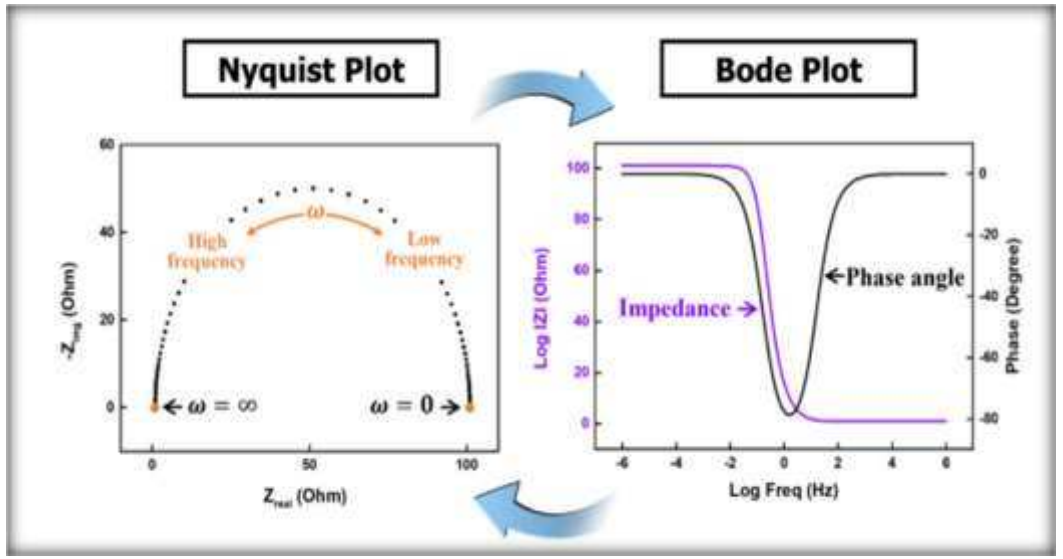
Corrosion test time	Polyurethanes	Rp	CR, mpy
Before corrosion test	No additive	318 Mohm	10.61 $x10^{-6}$
	With zinc phosphate	440.7 Mohm	6.64 $x10^{-6}$
	With ınhibisphere A	545.3 Mohm	5.98 $x10^{-6}$
	With ınhibisphere ZS	48.05 Mohm	47.87 $x10^{-6}$
	With cerium octoate	910.4 Mohm	2.177 $x10^{-6}$
After 500 hours corrosion test	No additive	1.01 kohms	2.642
	With zinc phosphate	1.456 kohms	1.557
	With inhibisphere A	2.405 kohms	0.28
	With inhibisphere ZS	0.27 kohms	4.85
	With cerium octoate	1 kohms	4.66

It is seen that the corrosion protection ability of Inhibisphere-ZS and Cerium octoate have the lowest value.

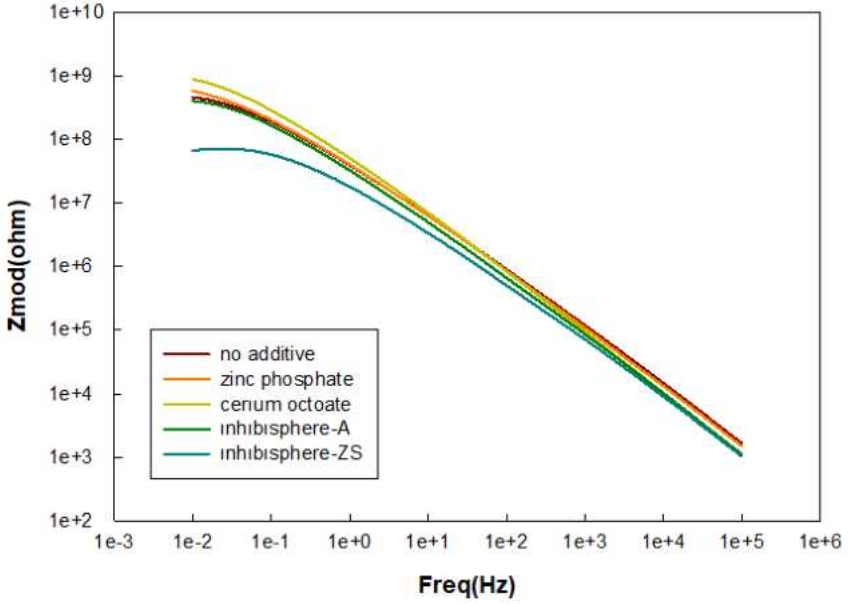
Bode and Nyquist Plots

- There are different ways to illustrate the response of an electrochemical system to an applied AC potential or current.

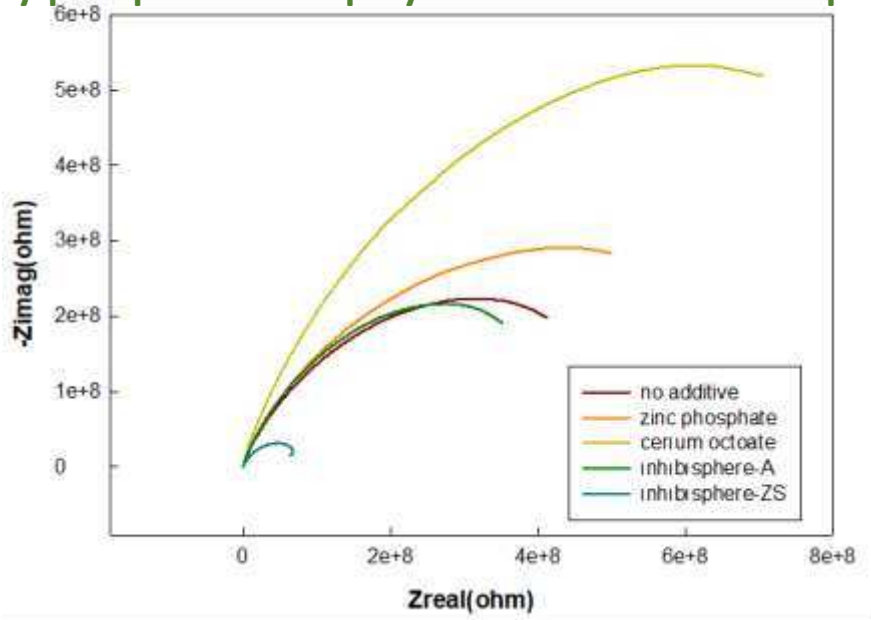
- The most common plots are the Nyquist plot and Bode plots.



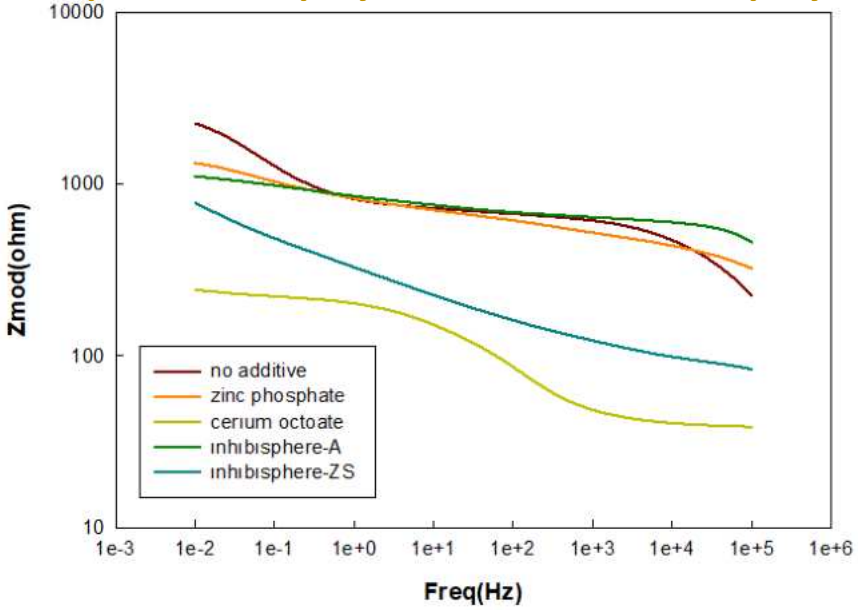
Bode plots of the polyurethanes before salt spray test



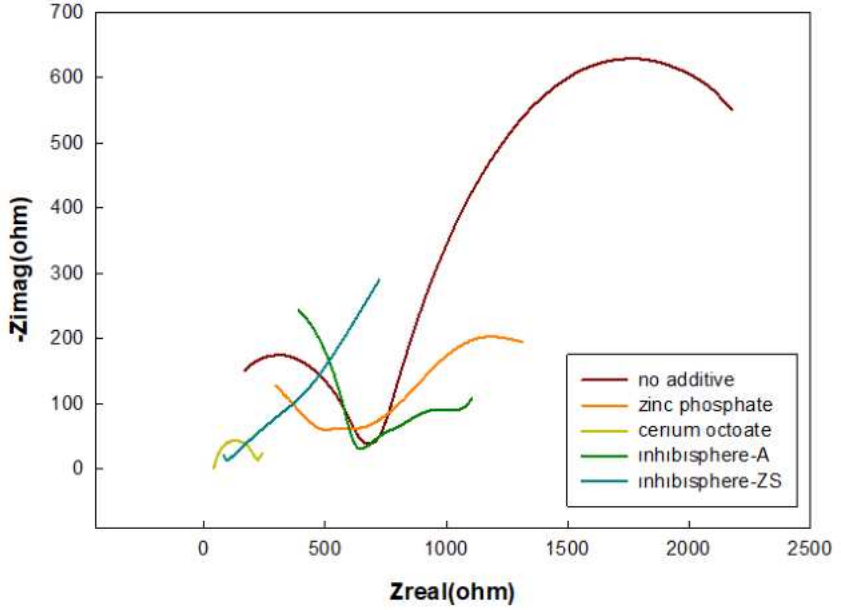
Nyquist plots of the polyurethanes before salt spray test



Bode plots of the polyurethanes after salt spray test



Nyquist plots of the polyurethanes after 500 hours salt spray test



Bode and Nyquist Plots

- **The goodness of fit values and EEC models of the two selected different models are as follows.**

Table 7: Goodness of fit values for two selected EEC models

EEC Models	Goodness of fit value
MODEL 1	3.34×10^{-2}
MODEL 2	7.51×10^{-6}

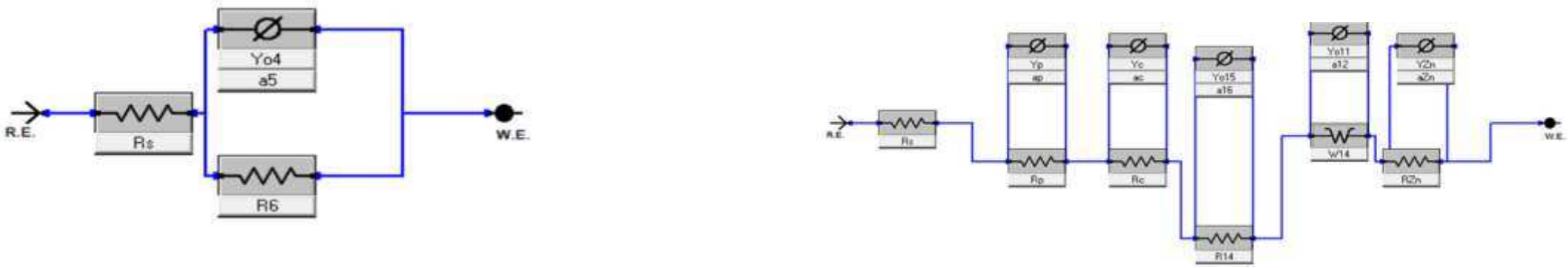


Figure 8: The equivalent electric circuits for MODEL 1,MODEL 2

Pore Resistance (Rp) and Coating Resistance(Rc)

- The protection behaviors off all the coatings are discussed in terms of Rp (pore resistance) and Rc (coating resistance).

Table 8: The pore resistances (Rp) and coating resistances (Rc) for different coatings before and after 500 hours salt spray test

Corrosion test time	Polyurethanes	Rp (ohm)	Rc (ohm)
Before corrosion test	No additive	$32.11x10^6$	$61.02x10^6$
	With zinc phosphate	$342.1x10^6$	$247.6x10^6$
	With ınhibisphere A	$473.2x10^6$	$330x10^6$
	With ınhibisphere ZS	$0.084810x10^6$	$1.532x10^6$
	With cerium octoate	$0.083860x10^6$	$300.1x10^6$
After 500 hours corrosion test	No additive	120,1	300.2
	With zinc phosphate	134,1	385,5
	With ınhibisphere A	611,8	550.8
	With ınhibisphere ZS	78,89	8,7
	With cerium octoate	147,2	77,4

SEM ANALYSIS RESULTS

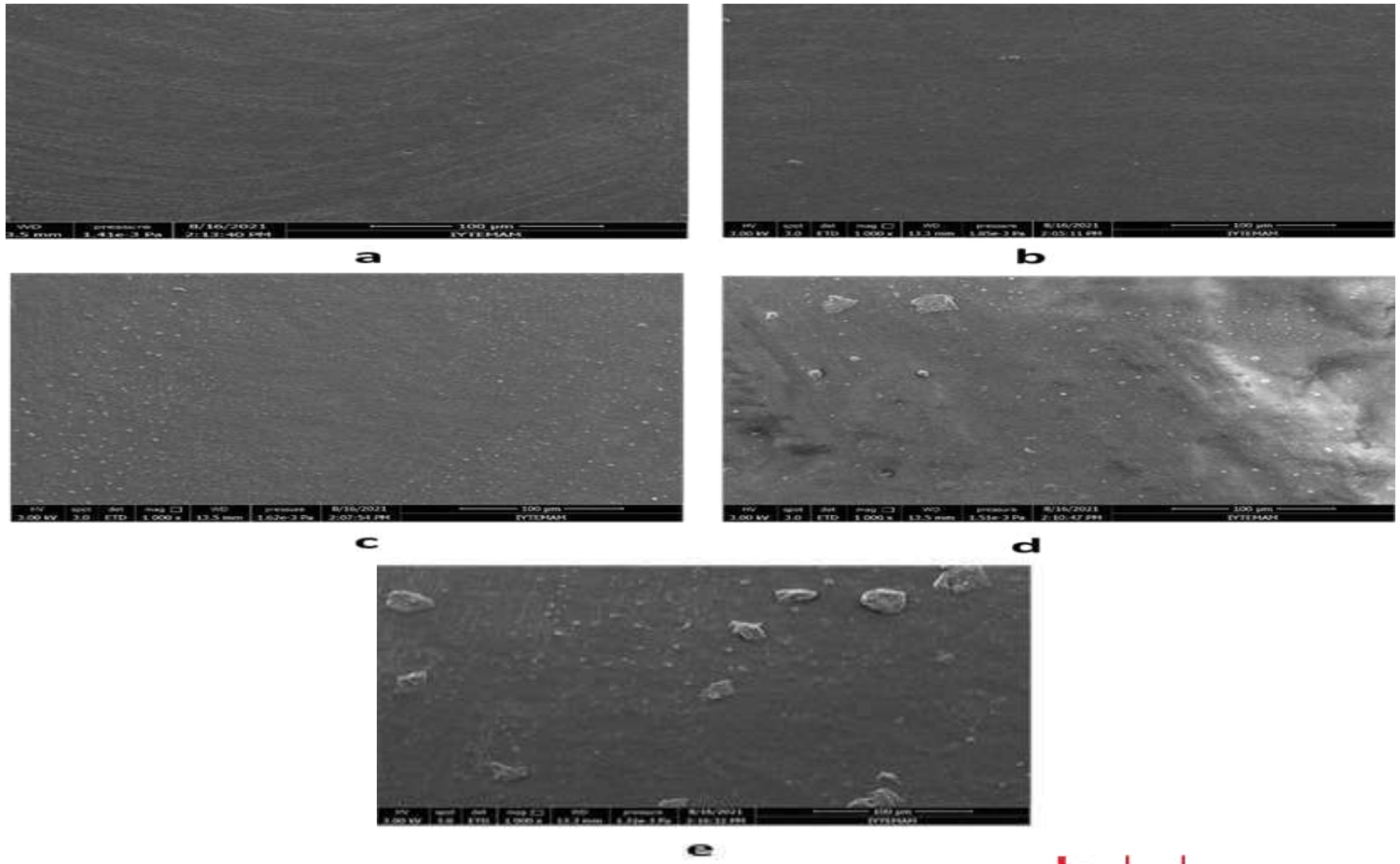


Figure 9:

a	No additive
b	Zinc phosphate
c	Inhibisphere A
d	Inhibisphere ZS
e	Cerium octoate

CHEMICAL RESISTANCE TEST

- For chemical resistance tests, the prepared film polyurethanes was completely immersed in the prepared solutions for 30 days.
- Used solutions and chemicals are as follows:

- %10 sulfuric acid (H_2SO_4),
- % 30 sodium chloride (NaCl),
- % 30 sodium hydroxide (NaOH)
- Diesel fuel

- After chemical resistance tests, all the PU films were affected as the loss in gloss and slight change in colour was observed against all chemical tests media (acid,alkali,nötral,diesel).

CHEMICAL RESISTANCE TEST

Table 9 : Alkali resistance test after 30 days (example)

Solutions and chemicals	Polyurethanes	Color change (ΔE)	Gloss loss (%) 20°	Gloss loss (%) 60°	Gloss loss (%) 85°	Weight change percentage (last weight-initial weight / initial weight) x100)
Sodium hydroxide (NaOH) (%30)	No additive	0.47	94.69	91.80	97.44	2.71
	Zinc phosphate	1.27	96.91	89.24	66.70	2.18
	Inhibisphere-A	0.84	69.09	46.97	14.78	0.81
	Inhibisphere-ZS	0.27	86.47	60.94	32.63	0.002
	Cerium octoate	0.14	86.93	50.11	21.21	-0.55

**As an example, only coating resistances in alkaline media are shown.

HARDNESS TEST

- **Persoz hardness values of five different polyurethane coatings are shown in table below.**

Table 10: Pendulum hardness test results

Polyurethanes	Pendulum hardness (Persoz)
No additive	118
Zinc phosphate	128
Inhibisphere-A	191
Cerium octoate	194
Inhibisphere-ZS	216

CONCLUSION

- **According to the 500 hours neutral salt spray results, the order of corrosion performance behavior is as follows:**

Inhibisphere-A>Zinc phosphate>No additive>Cerium octoate>Inhibisphere-ZS

- **The corrosion rates in miles per year by the Tafel method is as follows:**

Inhibisphere-A (0,171 mpy) < Zinc phosphate (1,493 mpy) < No additive (2,199 mpy) < Cerium octoate (4,178 mpy) < Inhibisphere-ZS (4,285 mpy)

- **As can be seen the chemical test results, the resistance of PU in alkali media (NaOH) was better gloss loss and weight differences than the other tested media (NaCl, H_2SO_4, Diesel fuel) due to the more urethane segments in their structures.**

- **The maximum persoz hardness value was found as 216 persoz (Containing Inhibisphere ZS). The variation of hardness values is as follows:**

Inhibisphere-ZS>Cerium octoate>Inhibisphere-A>Zinc phosphate>No additive

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