ANTICORROSION EFFICIENCY OF ZINC-FILLED EPOXY ESTER COATINGS CONTAINING CONDUCTING POLYMER PANI-PTSA

CoatEdge Dynamics

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AGENDA

- Introduction
- What is Corrosion?
- Anticorrosive coatings
- Goals of research
- Research work
- Conclusion
- Research paper
- Questions

INTRODUCTION

Research work focuses on development and testing of Organic Coatings for Corrosion protection of Metals.

Coatings are formulated with metallic pigments like zinc, conductive polymers.

Performance tests such as mechanical and corrosion tests are done to check efficiency of coatings

What is corrosion?

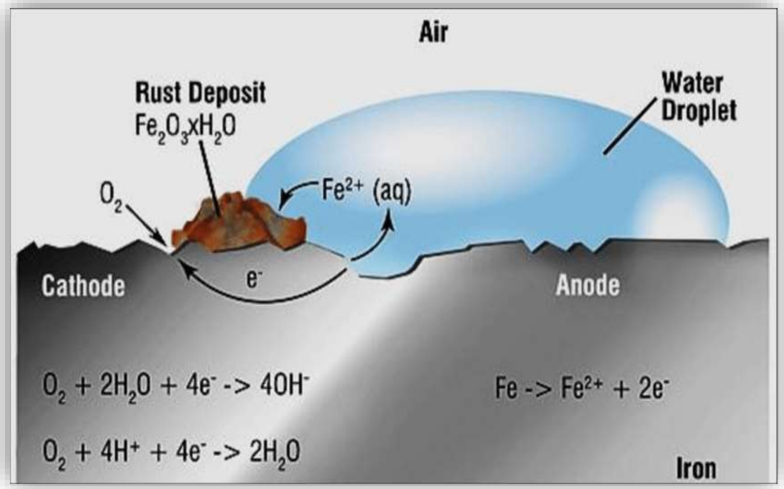
Corrosion is process of degradation of Metals, Concrete, Plastic or any material under influence of external environment.

External environmental factors can be natural or manmade.

Some of the substances corroding metals are:- Moisture, Oxygen, Acids, Sea Mists, CO_2, NO_2, NO, SO_2 and many industrial exhausts.

Corrosion of metals can be devastating, Economical loss due to corrosion globally is around 2.5 trillion USD.

Corrosion can be prevented by applying Anticorrosive coatings.



impact.nace.org/economic-impact.aspx

WHAT IS ANTICORROSIVE COATING?

- Carbon Steel Structures get Corroded because of Surrounding Environment.
- Coatings Protect Structures from Corrosion by forming a layer over substrate.
- Depending on application area, chemistry and substrate, there are different categories of coatings
- Generally, Zinc dust is used as metallic pigment for Corrosion protection. As Zinc provides cathodic protection.
- Zinc rich coatings are widely used in industrial applications.

Protective coatings for structural steel – newsteelconstruction.com
Uncoated Weathering Steel Reference Guide | American Institute of Steel Construction (aisc.org)

GOALS

01

Study 1 Coatings with Zinc – To find optimum dosage of zinc. (Standard)

02

Study 2 Coatings with zinc and Polyaniline – To find optimum dosage of conductive polymers and zinc in combination

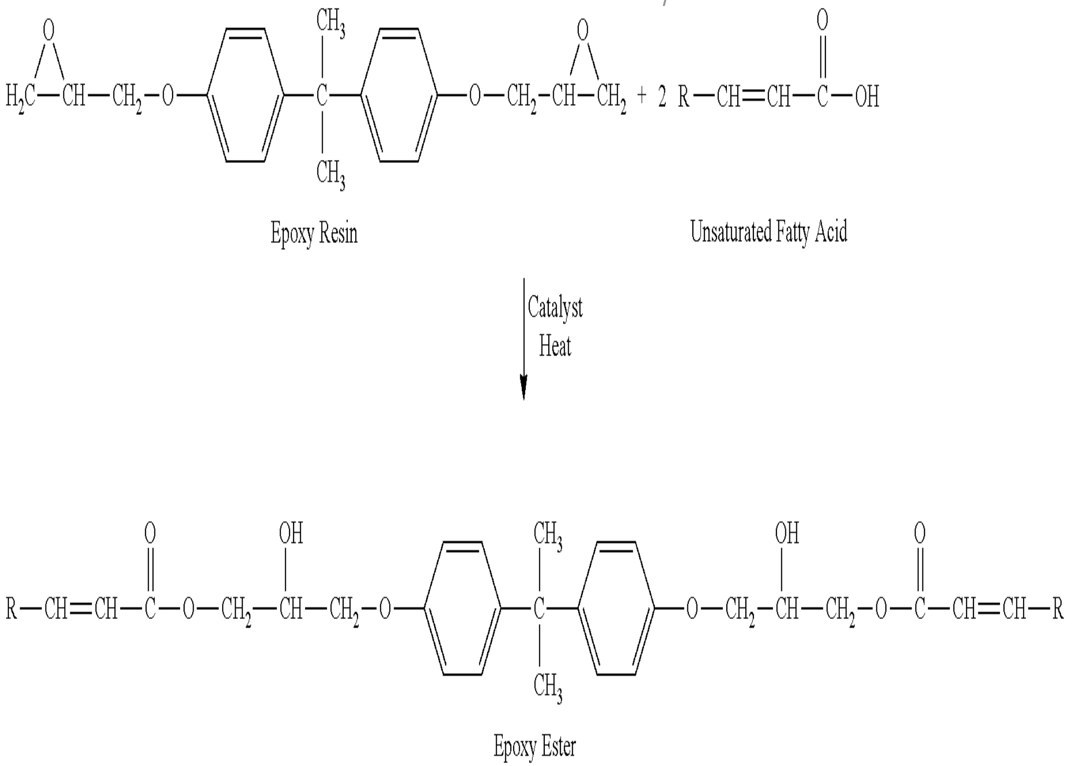
EPOXY ESTER

BPA-based epoxy resins can be converted into epoxy esters, i.e. products of the reaction between fatty acids and epoxy resins.

Epoxy esters are important resins for high-grade primers and fillers in industrial coatings.

The outstanding wet adhesion and the excellent corrosion protection of epoxy ester coatings are significant in extremely thin primer layers.

The humidity resistance and the highly durable adhesive bonds of epoxy coatings on metals, the high mechanical, chemical and thermal stability are the main reasons for the successful use of epoxy esters.



Chemical structure of epoxy ester, where R is the aliphatic chain.

ZINC PIGMENT

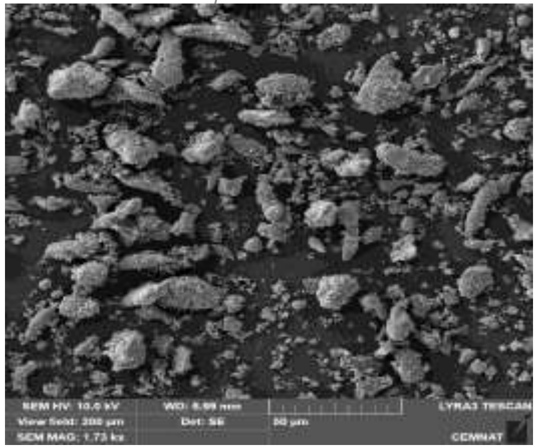
Metallic zinc powder pigment are used for superior corrosion protection in anticorrosive coatings.

Advantage of zinc is its tendency to protect steel substrate by sacrificial method. The zinc particles sacrifice themselves to give cathodic protection to the underlying substrate.

Usually, in formulation of paint zinc concentration is kept as high as 60-70& by weight of total paint.

Zinc powder is made from grinding zinc metal and reducing its particle size making spherical shape powdered pigment.

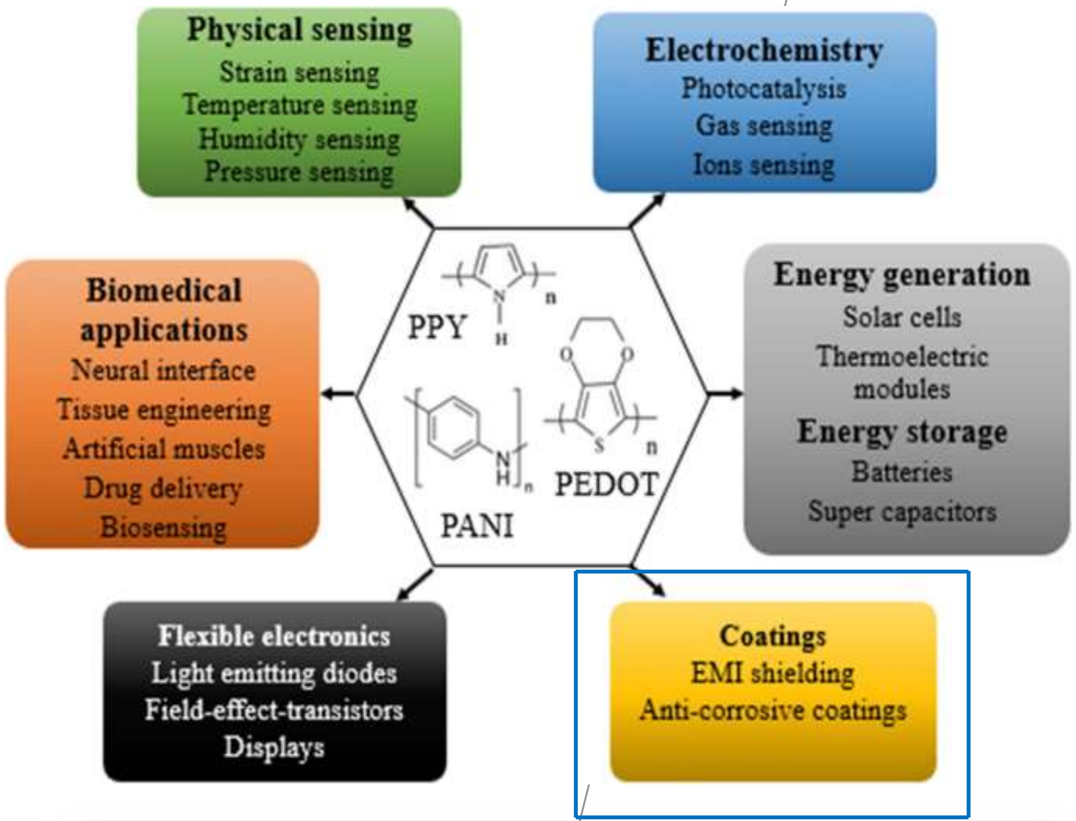
Zinc has higher negative electrode potential than iron, hence in presence of corrosive atmosphere zinc reacts first acting as anode and protects iron by making it cathode.

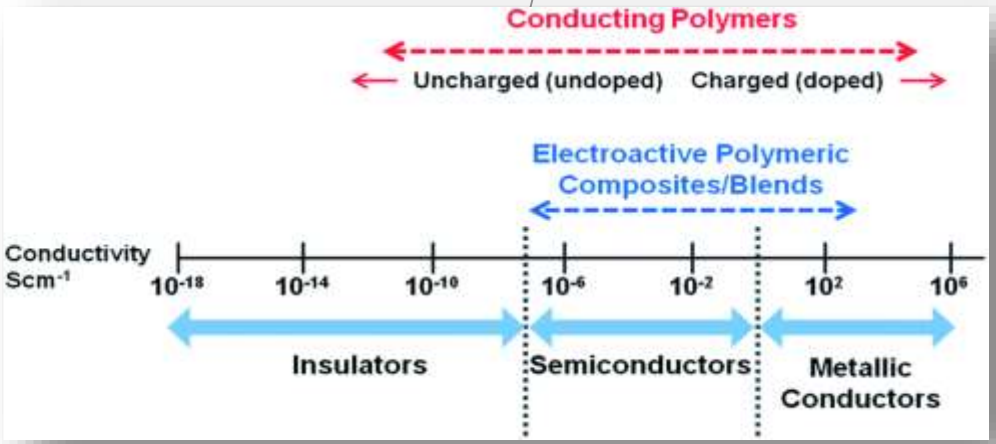


NEW DEVELOPMENTS

➢ **Conductive polymers**

- Conductive Polymers are synthesized organic compounds that possess conductivity or are semiconductors.
- Use of conductive polymers in corrosion Protective Coatings to increase efficiency.
- Used to replace concentration of Zinc in Coatings.
- Conductivity in Range of 10^{-2} to 10° (S/cm).
- Types of conductive polymers are polyaniline, polythiophene, polypyrolle, polyethylene.





Gagan Kaur ,, Raju Adhikari , Peter Cass , Mark Bown and Pathiraja Gunatillake, Electrically conductive polymers and composites for biomedical applications

POLYANILINE SALTS

Polyaniline Salts were synthesized in lab at room temperature.

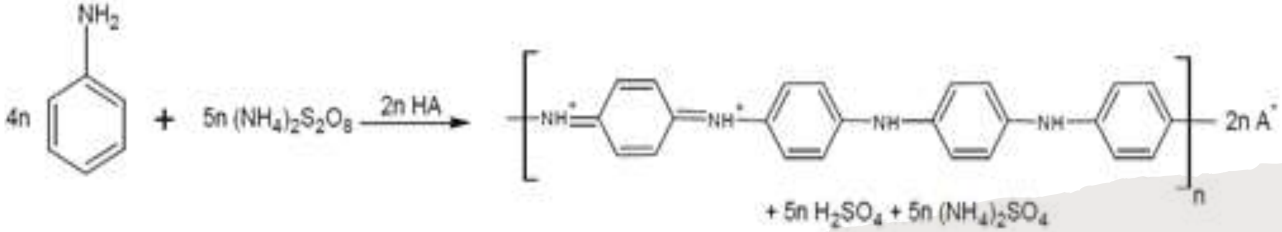
Raw materials used were Aniline, Phosphoric acid, PTSA, Ammonium Peroxidisulphate and water.

Reaction is carried out for 1 hour.

Then the material in kept at room temp for 24 hours after which it is washed and filtered.

Conductive polymers are air dried, and oven dried for 24hrs each.

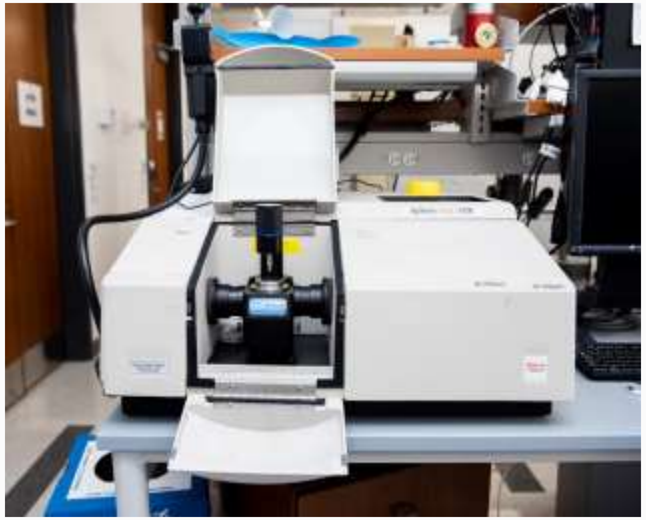
Resultant Polymeric Pigments were grinded to obtain optimum particle size.



CHARACTERIZATION

SEM – Scanning Electron Microscopy

FTIR spectroscopy

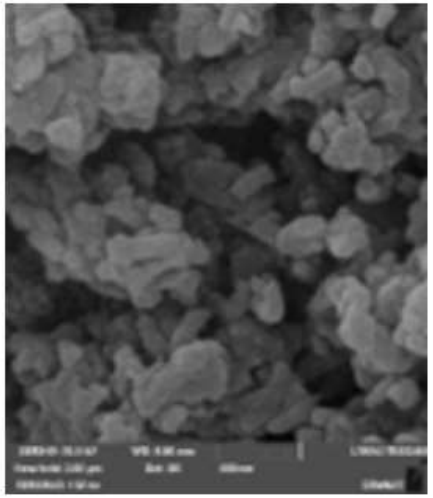


XRD – X ray diffraction

CHARACTERIZATION

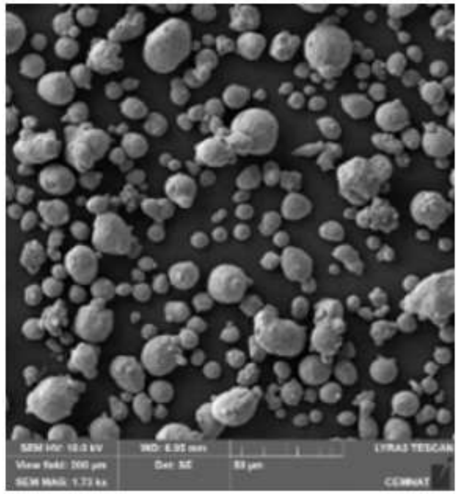
SEM

- SEM images of PANI-H_3PO_4, PANI-PTSA and Zinc are shown in figure
- Zinc has spherical shape
- PANI salts has irregular shape



Particle Size- 4.0±0.1 µm

PANI-PTSA

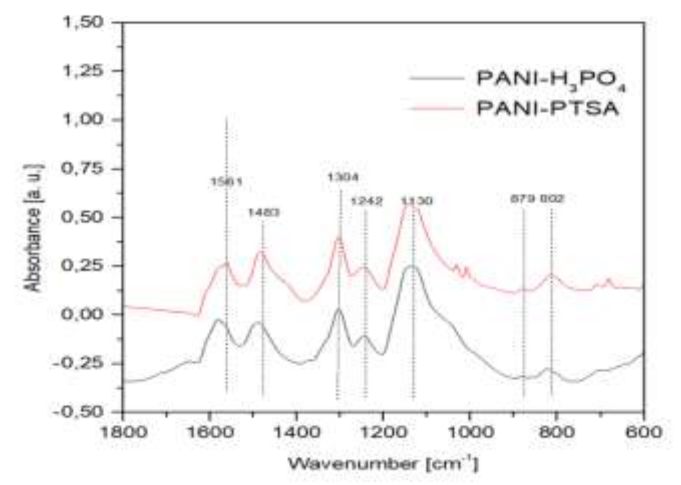


Particle Size- 4.7±0.1 µm

Zinc

CHARACTERIZATION

FTIR spectroscopy



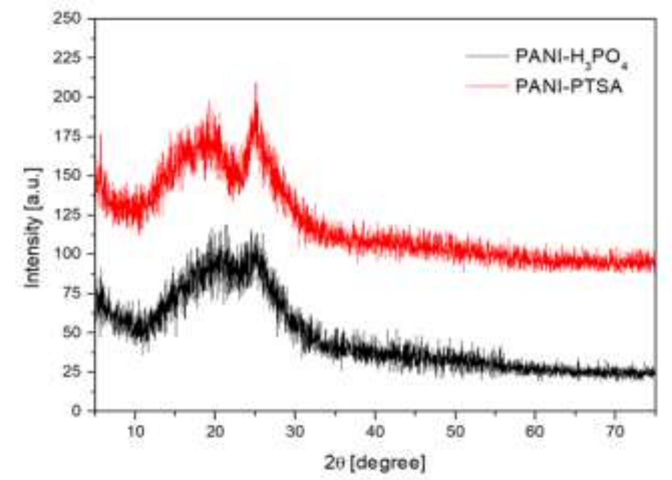
The chemicals were investigated using FTIR spectroscopy in the 4000-600 cm^{-1} range. All the polyaniline samples that were generated displayed medium bands at 3449, 3231, and 3060 cm^{-1} that, respectively, corresponded to the stretching vibrations of the OH, NH, and aromatic CH bonds.

The spectra of polyaniline salts are shown in Figure 10 in the 1800–600 cm^{-1} range, where bands typical of polyaniline salts are found

In the PANI-PTSA, weak absorption at 1373 cm^{-1} was found, typical of the polyaniline base (C–N stretching in the neighborhood of a quinonoid ring). The presence of this band indicates that the polyaniline salt was not fully protonated, which also correlates with the lower conductivity observed for these two samples.

CHARACTERIZATION

XRD – X ray diffraction



- PANI-PTSA has three peaks at 2θ around 14°, 20°, and 25°, as shown in the graph.
- The branches of the doping agents that were added to the polyaniline chains at various points may be responsible for the other peaks.

CHARACTERIZATION

Density, CPVC and oil number of pigments

Gas pycnometer

- Studies pigments were tested under gas pycnometer to obtain value of density.
- From density values, oil absorption and critical pigment volume concentration were calculated.
- Oil absorption – It is an amount if linseed oil required to wet all the particles in 100 gm of pigment. It gives idea of resin intake of pigment
- CPVC – CPVC is the abbreviation for critical pigment volume concentration. CPVC is the pigment concentration where the pigments are packed as close as possible and the binder is exactly the amount required to fill the space between the pigments.

Pigment	Density [g.cm^{-3}]	Oil number [g/100 g pigm.]	CPVC
Zinc	7.09	7	65
PANI-PTSA	1.41	74	47

Temperature-controlled gas pycnometer | Laboratory Talk

CHARACTERIZATION

Molecular weight and electrical conductivity of polyaniline salts

- Determination of molecular weight
  - Gel permeation chromatography
    - N-Methylpyrrolidon / LiBr
- Determination of electrical conductivity
  - Specific Resistance Measurement
    - Van der Pawn

Polyaniline salt	M_w	M_w/M_n	Conductivity [$S.cm^{-1}$]	Particle size [µm]
PANI-PTSA	25,000	4.8	5.85	3.9 ± 0.1

- **Kalendová, I. Sapurina, J. Stejskal, D. Veselý,** Anticorrosion properties of polyaniline-coated pigments in organic coatings. *Corrosion Science 50*. 2008, pp. 3549-3560

A. M. Kohl, A. Kalendová, J. Stejskal, The effect of polyaniline phosphate on mechanical and corrosive properties of protective organic coatings containing high amounts of zinc metal particles, *Progress in Organic Coatings*, 77, 2. 2014, pp. 512-517.

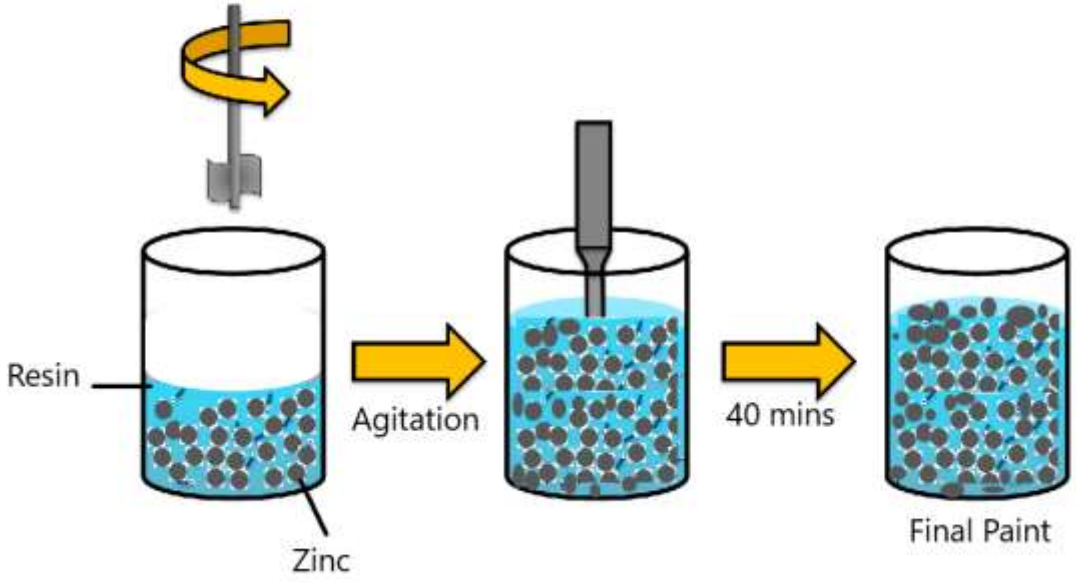
COATING SYNTHESIS

- ZINC RICH COATINGS WERE SYNTHESIZED BY USING EPOXY ESTER RESINS.
- COATINGS WERE PREPARED IN DISSOLVER AT 1300-1500 RPM FOR 40 MINS.
- GLASS BEADS WERE USED AS GRINDING MEDIUM.
- VARIOUS BATCHES WITH DIFFERENT COMBINATIONS WERE PREPARED.

FORMULATION

Study 1 Coatings with Zinc

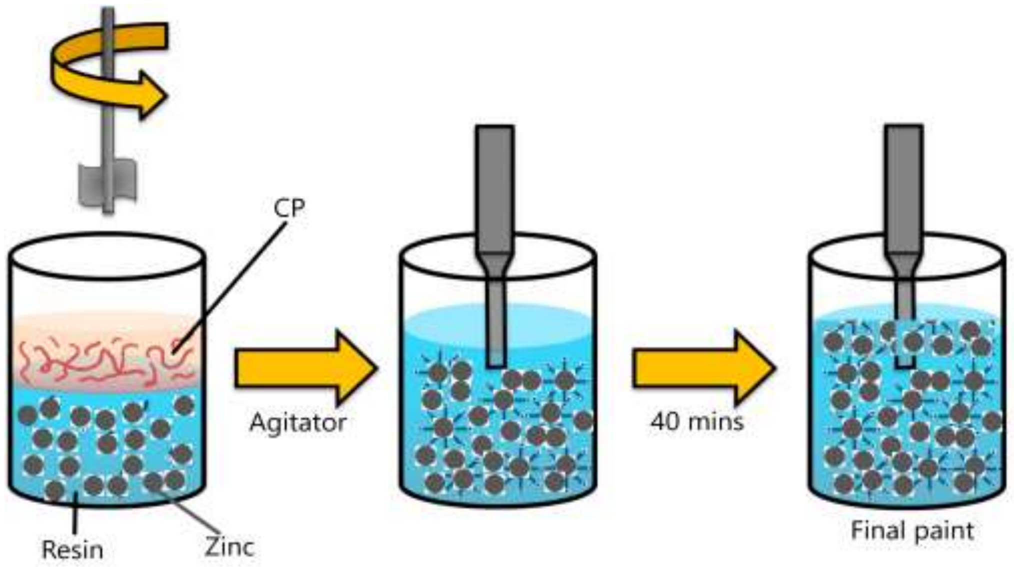
Samples	Resin	Zinc	CaCO3
Zn PVC 0	45.7	0	54.3
Zn PVC 1	45.37	1.32	53.31
Zn PVC 3	44.66	3.8	51.54
Zn PVC 5	43.04	9.61	47.35
Zn PVC 10	40.39	19.02	40.59
Zn PVC 15	37.74	17.4	33.96
Zn PVC 20	35.21	37.32	27.47
Zn PVC 25	32.68	46.24	21.08
Zn PVC 30	30.21	54.98	14.81
Zn PVC 35	27.8	63.53	8.67
Zn PVC 40	25.42	71.94	2.64
Zn PVC 45	22.37	77.63	0



FORMULATION

Study 2 Coatings with zinc and polyaniline

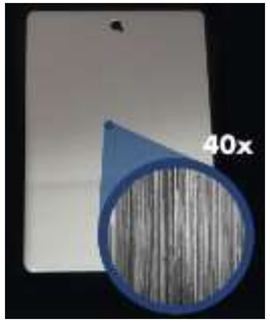
Samples PANI-PTSA	Resin	PANI-PTSA	Zinc	CaCO3
Zn PVC 1	46.37	1.2	2.11	50.32
Zn PVC 10	42.77	1.11	14.54	41.58
Zn PVC 20	36.99	0.96	34.38	27.67
Zn PVC 30	31.54	0.82	53.2	14.44
Zn PVC 40	26.35	0.68	71.07	1.9
Zn PVC 50	19.47	0.5	80.02	0
Zn PVC 60	13.78	0.36	85.86	0



Application

Applicator

DFT meter



Steel panel

- Coatings were applied by using standard applicator
- Application was done by applicator slid.
- Glass panel was applied with WFT 150µm and Steel panel was applied with WFT 300µm
- The dry film thickness (DFT) was measured with a magnetic gauge according to ISO 2808.

PERFORMANCE TESTING

Salt spray test

- Accelerated cyclic corrosion test in an atmosphere of NaCl with water steam condensation (derived from ISO 9227).
- Tests were conducted in a testing chamber (SKB 400 A-TR-TOUCH, Gebr. Liebisch GmbH & Co. KG, Germany) over the course of three 12-hour cycles: 10 hours of exposure to a mist of 5 % NaCl solution at 35 °C; 1 hour of exposure at 23 °C; and 1 hour of humidity condensation at 40 °C. The samples were subjected to these conditions for 120, 240, 480, and 960 hours before evaluation.

Salt Spray Test Equipment | Fog Chamber | Cyclic Corrosion (aresscientific.com)

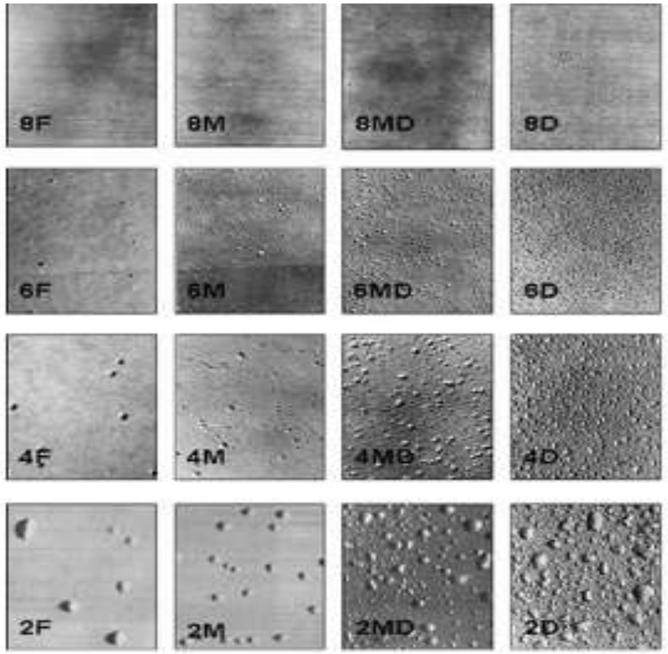
PERFORMANCE TESTING

Physical-Mechanical test

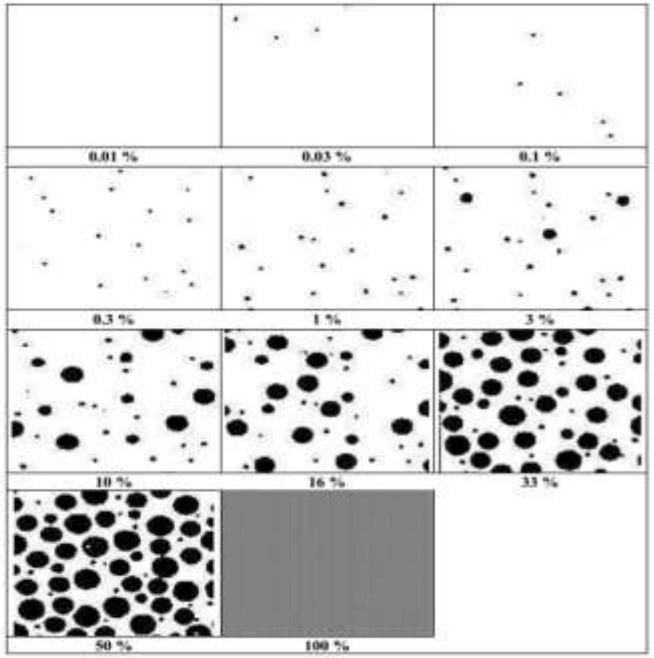
- By slicing a lattice into the films in line with ISO 2409, the adherence of the films to the substrate was assessed using a specific cutting blade with cutting edges separated by 2 mm.
- 1000 g weight was dropped upon steel panels, and the largest height (in mm) at which the film integrity remained unaffected was noted (ISO 6272) for impact resistance.
- The cupping test was assessed using measurements made on a cupping tester. The depth of the steel ball indentation (in mm) at which the integrity of the film was not jeopardized, according to ISO 1520.
- According to ISO 1519, painted panels are bent over mandrels of varying diameters to test the material's flexibility and record the maximum diameter (in mm) at which the paint film is not fractured.
- The pull-off test for adhesion was measured in accordance with ISO 4624.

Conical mandrel bend tester | Rycobel
Manual Adhesion Tester Positest AT, ATM20A, ATM50A, ASTM D4541 (checkline.com)
TQC Sheen Cross Cut Adhesion Test KIT CC2000 - Industrial Physics
Impact tester for paint — Neurtek

Evaluation of corrosion after the corrosion test.



ASTM D 610-85 photographic standard for corrosion in the surface of the substrate



ASTM D 714-87 Blister Evaluation Photographic Standards

Results of Study 1
Zinc coatings

Results of salts spray test

after 800 hrs. exposure, DFT = 90±10 µm

Study of organic coatings with Zinc

Samples	% corrosion on the metal surface
45% Zinc	3
40% Zinc	3
30% Zinc	10
20% Zinc	10
10% Zinc	16

Samples	Blisters in Cut [dg.]	Blisters in Surface [dg.]
45% Zinc	8M	8F
40% Zinc	8M	4F
30% Zinc	8M	8F
20% Zinc	8MD	8F
10% Zinc	2F	8F

- Zn PVC 45 shows least corrosion
- Blistering was also observed less with Zn pvc 45
- Low level of PVC (10-30) shows blistering and more corrosion
- Best electrical contact of zinc particles is achieved at PVC 45. Hence, excellent performance is observed

45% Zn PVC

30% Zn PVC

RESULTS OF MECHANICAL TEST

Study of organic coatings with Zinc

Zn PVC	Adhesion	Cupping	Flexibility	Hardness – konig (sec)	MEK rub (sec)
Zn 10	5B	>10 mm	5 mm	38	80
Zn 20	5B	9.8 mm	5 mm	39	82
Zn 30	5B	9.65 mm	5 mm	42	117
Zn 40	5B	9.2 mm	5 mm	42	93
Zn 45	5B	9.1 mm	5 mm	44	85

- Cross cut adhesion test gives almost identical results.
- Coatings with all Zinc PVC gives excellent adhesion.
- Flexibility of all the zinc coating was observed similar
- All zinc coatings underwent flexibility test at 5 mm bent successfully

- Cupping tests checks the stretching capacity of coating.
- As from table, lower dosage of zinc has better cupping resistance.
- Higher concentration of zinc results in decrease in cupping resistance due to higher solid content and lower binder content.

- As it is observed from table, Zn PVC 45 has maximum hardness
- Lower the dosage of zinc, hardness is low
- This can be explained by packing efficiency of zinc as a metallic pigment.

- As it is observed from table, MEK rub is maximum obtained with Zn PVC 30
- Lower the dosage of zinc, has poor MEK resistance because if insufficient zinc present
- Higher concentration of zinc leads to less binder which results in lower MEK resistance.

CONCLUSION OF STUDY 1

Lower dosage of zinc 5-30

When Zinc dosage is kept low, there is no sufficient contact between zinc particles for cathodic protection, hence corrosion protection is not achieved.

Lower dosage of zinc 5-30

Keeping optimum dosage of zinc in coatings offers best cathodic protection as well as improved mechanical properties.

Higher dosage of zinc 50-60

Increasing dosage of zinc in coatings leads to creation of pores which allows penetration of corrosive substances through the coating to substrate.

Results of Study 2
Zinc and polyaniline coatings

Results of salts spray test

after 800 hrs. exposure, DFT = 90±10 μm

Study of organic coatings with Zinc and PANI

Samples	% corrosion on the metal surface
Zn PVC 10	16
Zn PVC 20	33
Zn PVC 30	3
Zn PVC 40	10
Zn PVC 50	50

Samples	Blisters in Cut [dg.]	Blisters in Surface [dg.]
Zn PVC 10	6D	6D
Zn PVC 20	8D	8D
Zn PVC 30	8M	8D
Zn PVC 40	8D	6D
Zn PVC 50	8D	8D

- Zn PVC 30 and 40 shows least corrosion with PANI-PTSA PVC 3.
- Blistering was also observed less with Zn PVC 30.
- High level of Zn PVC (40-50) shows blistering and more corrosion
- Best electrical contact of zinc particles is achieved at Zn PVC 30 and PANI-PTSA PVC 3. Hence, excellent performance is observed.

ZINC PVC 30% + PANI-PTSA PVC 3%

Zinc PVC 45%

RESULTS OF MECHANICAL TEST

Study of organic coatings with Zn and CPs content

Results of the mechanical properties of the studied PANI-PTSA coatings. DFT = 95±5µm.

PVC_{Zn}	Adhesion test [dg.]	Bend test [mm]	Impact test [cm]	Cupping test [mm]	Pull-off strength [MPa]	Fracture type [%]	Flexibility	Hardness – konig (sec)	MEK rub (sec)
10	5B	5	> 100	7.6	0.7	B	5 mm	44	106
20	5B	5	> 100	8.3	0.7	B	5 mm	46	127
30	5B	5	> 100	8.2	0.6	B	5 mm	49	131
40	5B	5	> 100	> 10	0.8	B	5 mm	51	139
50	5B	5	> 100	> 10	0.5	B	5 mm	58	147

- Cross cut adhesion test gives best results for coatings with Zn PVC 30-50.
- Coatings with lower level of Zn fails in adhesion.

- Coatings with low level of zinc shows poor cupping resistance.
- Very high cupping resistance was observed with coatings with Zn PVC 40-50

- Flexibility of all the Zinc + PANI-PTSA coating was observed similar.
- All PANI coatings underwent flexibility test at 5 mm bent successfully

- Results from hardness tests shows maximum hardness at Zn PVC level 40-50 with PANI-PTSA PVC 3.
- Increasing the Zn PVC, hardness increases.

- MEK rub tests shows best results at Zn PVC 40 with PANI PVC 3.
- Increasing the PVC of Zinc, resistance to MEK is increased.

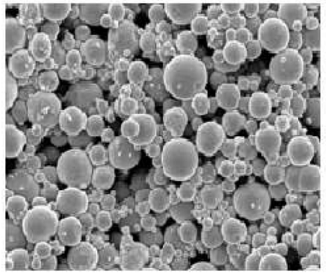
RESULTS OF LINEAR POLARIZATION

Study of organic coatings with Zn and CPs content

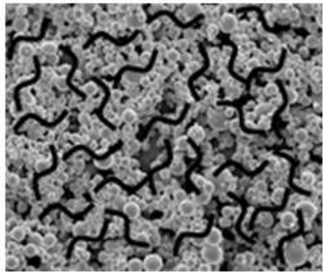
Results of the LP measurement of the studied PANI-PTSA coatings. DFT = 95±5μm

PVC_{Zn}	E_{corr} [mV]	I_{corr} [μA]	β_a [mV]	β_c [mV]	R_p [Ω]	$\upsilon_{corr.}$ [mm year^{-1}]
10	-960	$9{,}3x10^{-8}$	25,1	26,2	$7{,}0x10^{10}$	$1{,}4x10^{-9}$
20	-958	$5{,}4x10^{-8}$	26,6	23,8	$1{,}1x10^{11}$	$7{,}9x10^{-10}$
30	-955	$3{,}3x10^{-8}$	24,9	25,2	$1{,}9x10^{11}$	$4{,}9x10^{-10}$
40	-949	$1{,}4x10^{-7}$	26,3	27,7	$4{,}8x10^{10}$	$2{,}1x10^{-9}$
50	-946	$1{,}2x10^{-7}$	23,2	28,3	$4{,}9x10^{10}$	$1{,}7x10^{-9}$
60	-943	$3{,}1x10^{-7}$	24,5	29,1	$2{,}0x10^{10}$	$4{,}8x10^{-9}$

- Best values which give maximum polarization resistance and least corrosion rate were obtained with Zn PVC 20-40%.
- Coatings with Zn PVC 30% and PANI PVC 3% gives the best overall corrosion resistance which can be concluded from linear polarization test.
- Comparing the results of PANI-PTSA offers less corrosion rate and more polarization resistance. These results were noticeably similar to corrosion tests.
- Lower corrosion rate values for Zn PVC 30% and PANI-PTSA 3% is due to synergistic effect of corrosion resistance mechanism of both conductive polymer and metallic zinc.



a)



b)

SEM images of a) Zinc and b) Zinc infused with PANI

MECHANISM OF CORROSION PROTECTION

PANi pigment's superior redox property

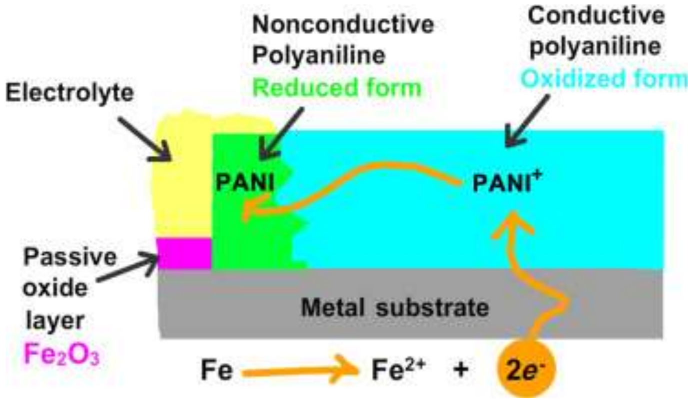
polyaniline cathodic reaction.

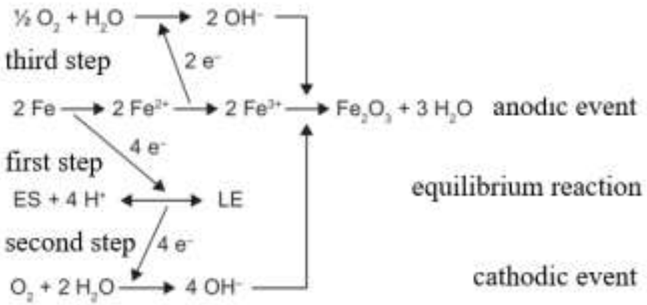
→ emeraldine salt (ES; oxidation state) form of polyaniline transferred to the reduced form of leucoemeraldine (LE; reduction state).

→ auto-oxidation of polyaniline, the reduction state (LE) of polyaniline could return to the oxidation state (ES).

→ increasing amounts of Fe_2O_3, Fe_3O_4 and ZnO deposited on the metal surface to form oxide passive films.

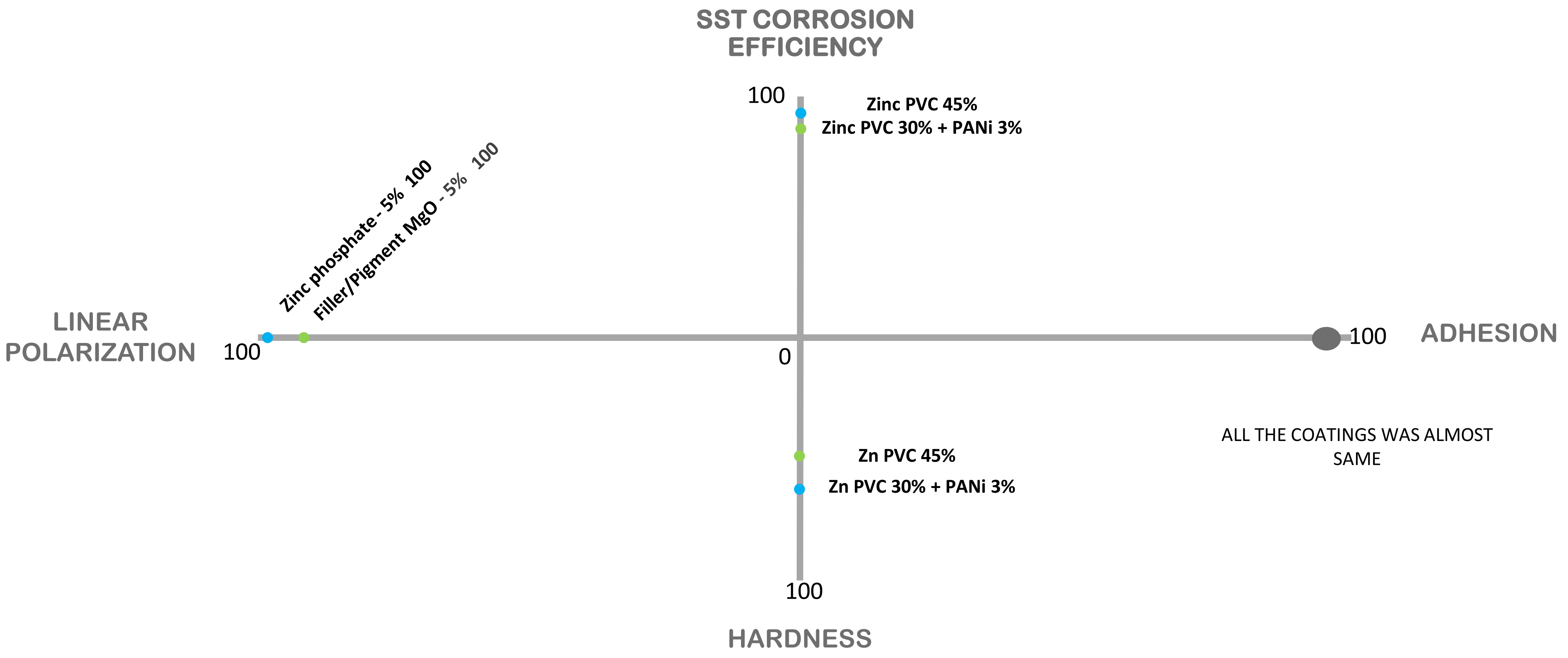
→ polyaniline, as a conducting polymer, acted as a "bridge" and filler to zinc particles, decreasing the coating porosity and enhancing the cathodic protection efficiency





Nedal Y. Abu-Thabit, Chapter 22 - Electrically conducting polyaniline smart coatings and thin films for industrial applications, Advances in Smart Coatings and Thin Films for Future Industrial and Biomedical Engineering Applications, Elsevier,

OVERALL RESULTS



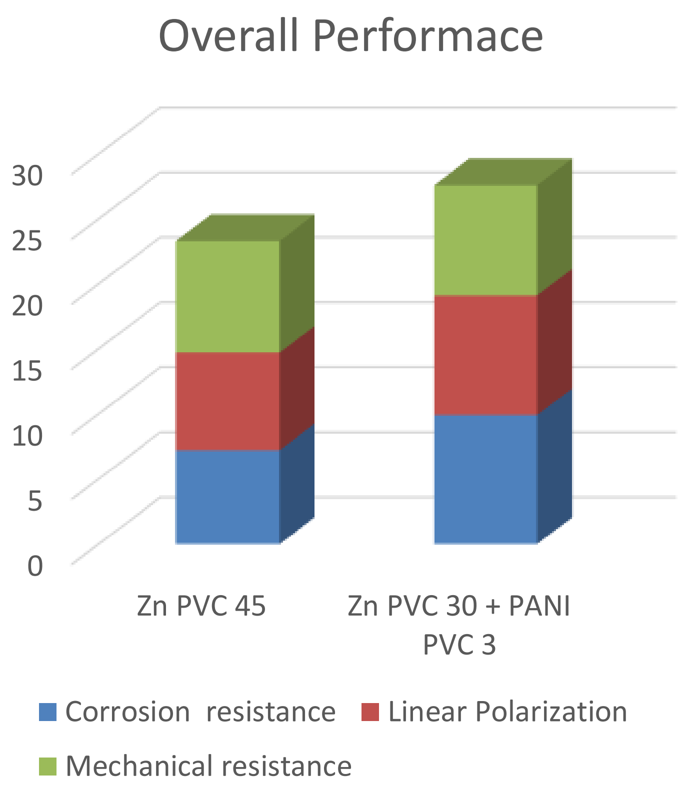
CONCLUSION OF STUDY 2

Zinc + Polyaniline para toluene sulphonic acid coatings

PANI-PTSA (PVC 3%) offers excellent corrosion protection with zinc at optimum dosage of Zn PVC 30%

Increasing the dosage of PANI does not improve performance but degrades it.

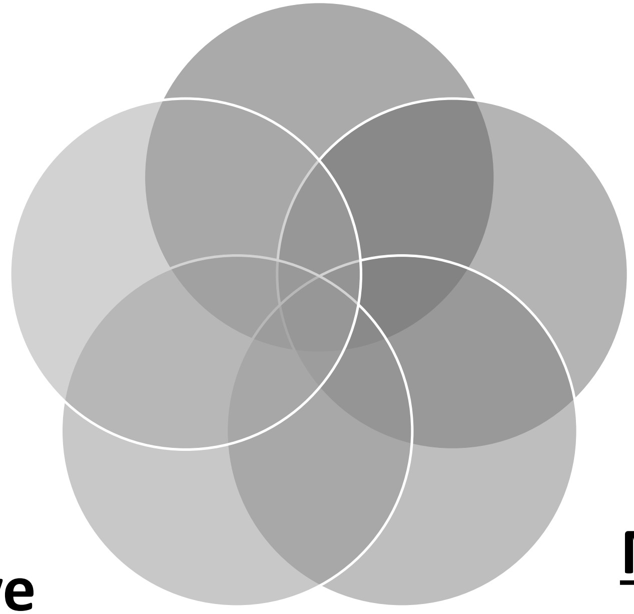
Excellent performance of PANI-PTSA is because of its high conductivity and less solubility.



FURTHER RESEARCH

Magnesium

Molybdinum sulphate



Aluminium

Organic anticorrosive pigment

Magnesium oxide

RESEARCH PAPER

Kohl, M.; Alafid, F.; Bouška, M.; Krejčová, A.; Raycha, Y.; Kalendová, A.; Hrdina, R.; Burgert, L. New Corrosion Inhibitors Based on Perylene Units in Epoxy Ester Resin Coatings. *Coatings* **2022**, *12*, 923. https://doi.org/10.3390/coatings12070923S

Yash Raycha, Miroslav Kohl, and Andréa Kalendová, Effect of concentration of zinc-powder in epoxy-ester based anticorrosive Coatings, Scientific Papers of the University of Pardubice, Series A; Faculty of Chemical Technology 29 (2023) 1–21. Accepted: June 28, 2023

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Thank you