SELF-HEALING WATERBORNE POLYURETHANE RESINS FOR ANTI-CORROSIVE PAINT APPLICATIONS

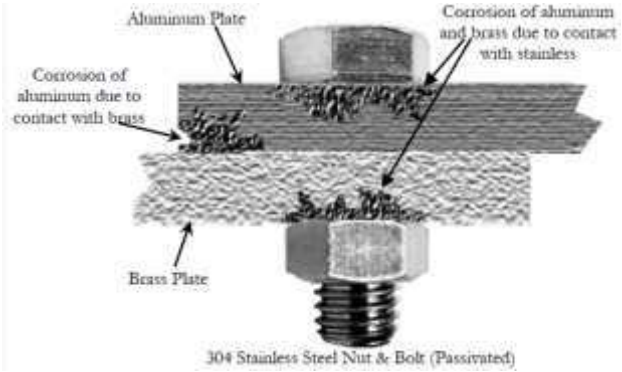
Mukaddes AYDIN
R&D Manager
Solvent Based Industrial & Decorative Coatings

Ekin Berksun [1], Soner Kızıl [2], Serkan Ünal [3], Yusuf Ziya Menceloğlu [4], Mukaddes Aydın [5]

CORROSION

Corrosion of metals (steel, aluminum, magnesium, etc.) is a major issue related to the economy:

- The total annual cost of corrosion is estimated as more than $310 billion in China,
- If the same ratio is applied to the global economy, the total annual cost will be approximately $2.5 trillion
- Anti-Corrosion Coating market size is forecast to reach $24.7 billion by 2026.



Journal of Magnesium and Alloys Volume 11, Issue 7, July 2023, Pages 2230-2259

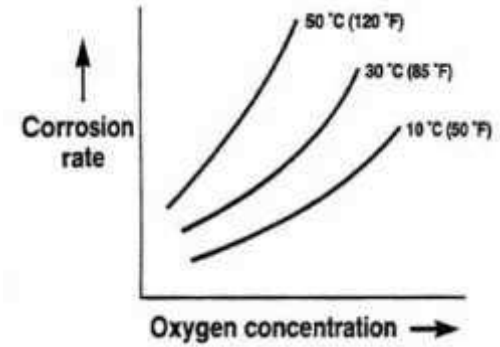
CORROSION

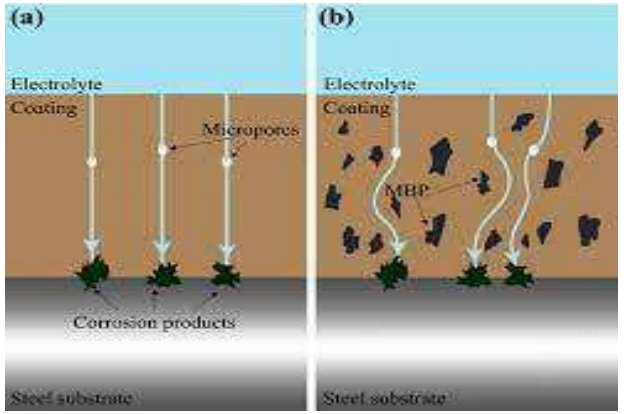
Corrosion is the loss of materials(metal and alloys) or its useful properties, by chemical or electrochemical interaction with its environment.

Corrosion of metals has a direct impact on reduced lifetime, reliability, and safety in microelectronics, construction, automotive, and aerospace applications, and is thus of significant economic and ecological importance.

Corrosion is enhanced by the prsence of

- İmpurities
- Air and moisture
- Electrolytes
- Strain in metals like dent, scratches etc.





Anticorrosion properties of modified basalt powder/epoxy resin coating *Journal of Coatings Technology and Research* **volume 19**, pages1409–1420 (2022)

SMART PROTECTIVE COATINGS

Hence, smart corrosion protection based on stimuli respon- sive release of suitably active agents is a highly important topic. Not surprisingly, there is an intense research carried out on that topic and the number of publications is steadily increasing over time as shown in Figure1.

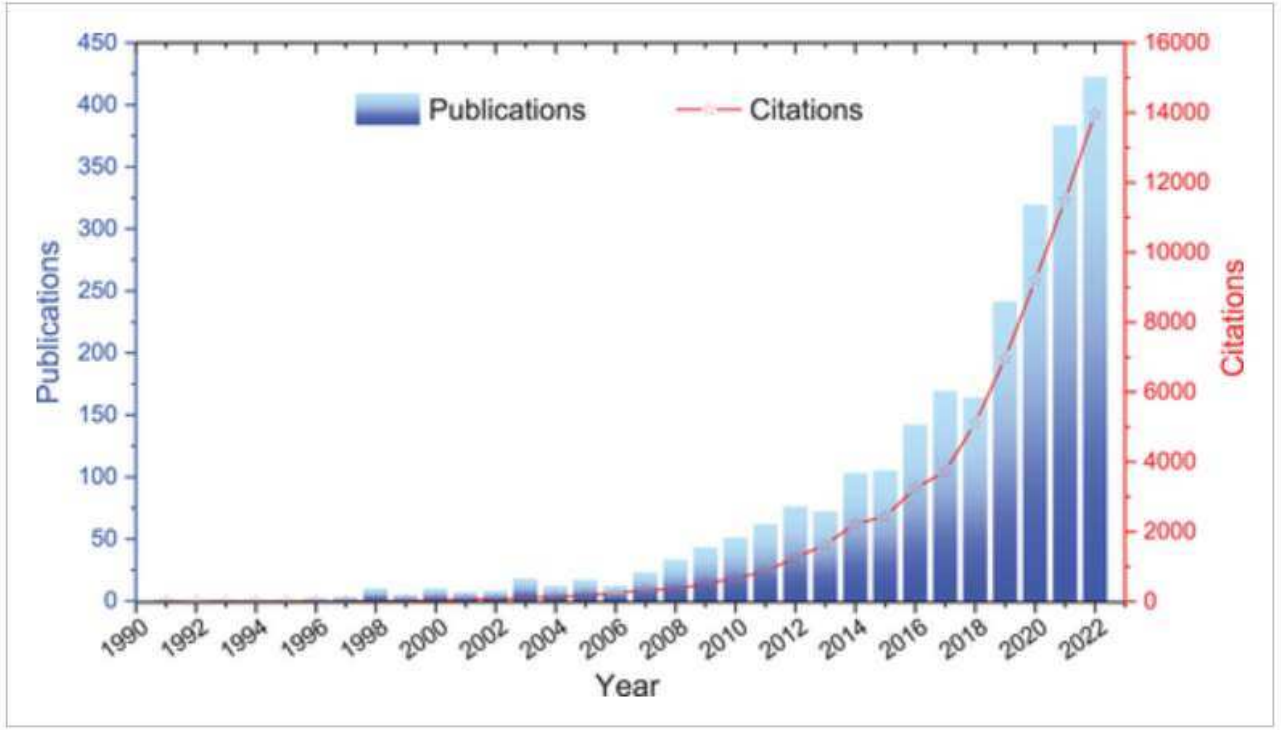
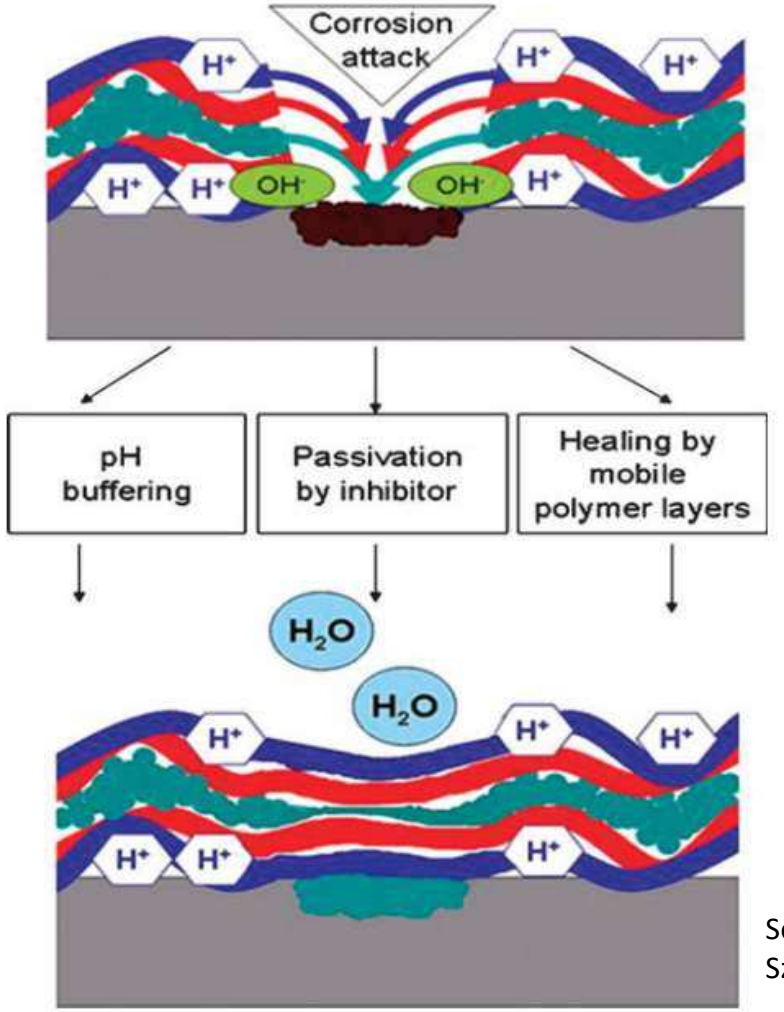


Figure1 Publications per years on smart self-healing coatings for corrosion protection

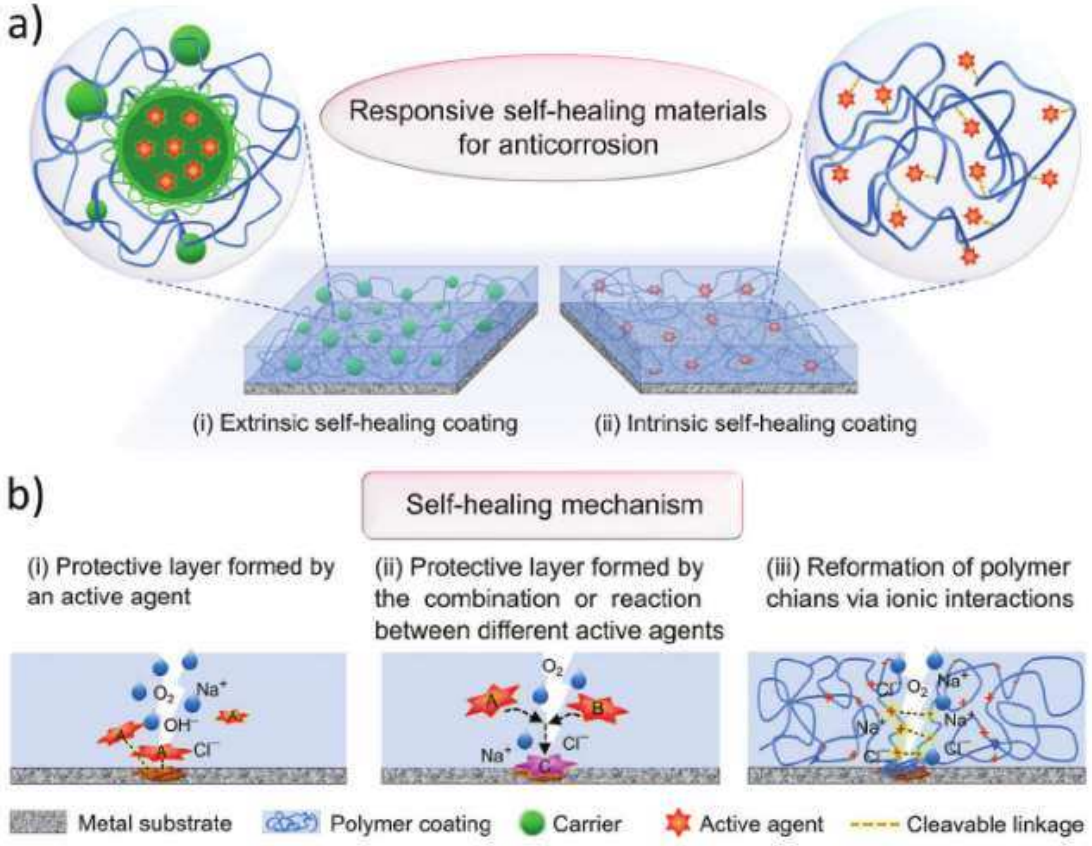
SMART PROTECTIVE COATINGS



- The addition of corrosion inhibitors directly to coatings, which is one of the possibilities of protecting a metallic substrate against the action of a corroding medium.
- The encapsulation of corrosion inhibitors and the introduction of the capsules into the matrix of the coating are considered to be a viable way of avoiding the above disadvantages.

Self-healing coatings in anti-corrosion applications Alicja Stankiewicz • Irena Szczygieł • Bogdan Szczygie, J Mater Sci (2013) 48:8041–8051 DOI 10.1007/s10853-013-761

SMART PROTECTIVE COATINGS

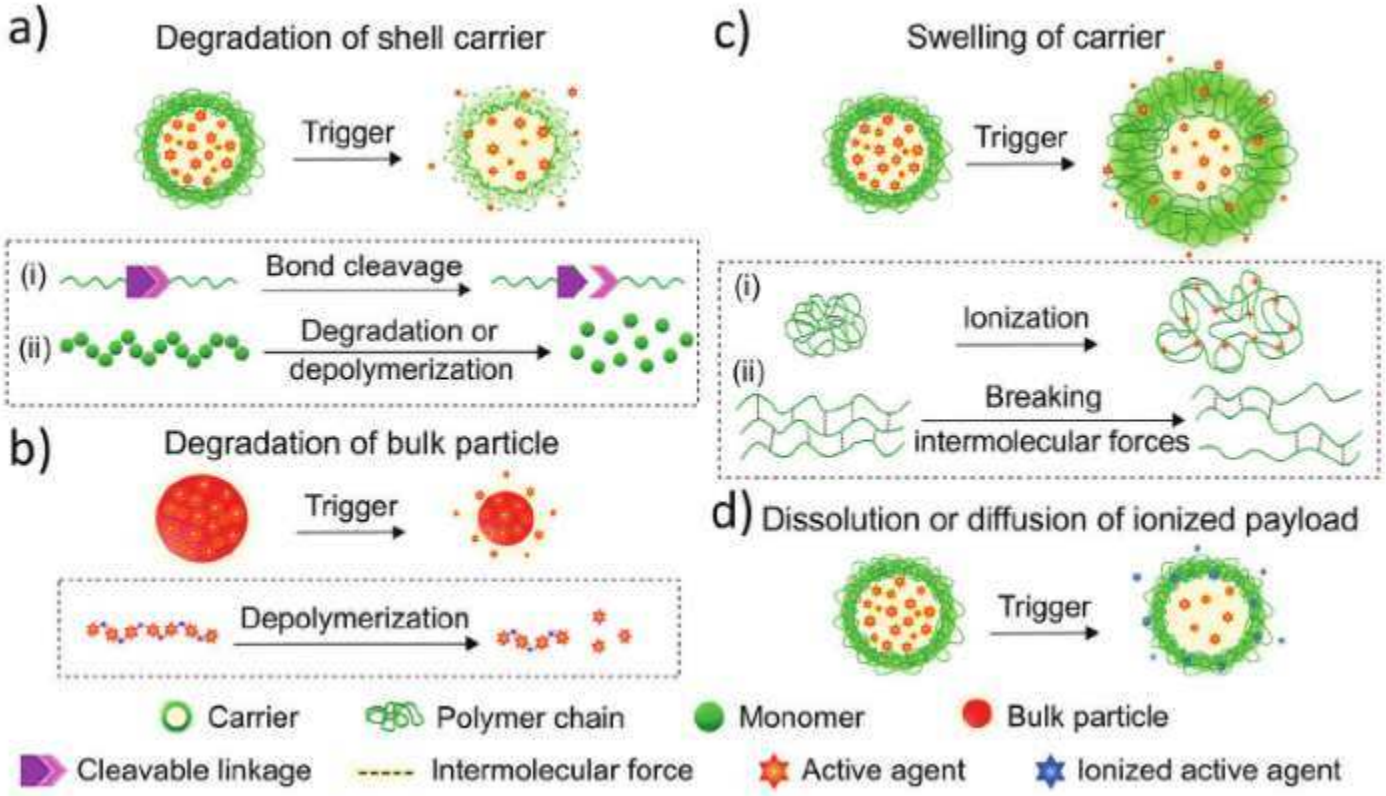


- a) Schematic illustrations for extrinsic (i) and intrinsic (ii) responsive self-healing materials for anticorrosion and

- b) self-healing mechanismof coatings for anticorrosion relying on the formation of protective layers, which are produced by an active agent (i),by the combination/reaction between two different active agents on corroded metal surfaces via chelation or physi- or chemisorption (ii), and by reformation of polymer chains via ionic interactions (iii).

Self-healing coatings in anti-corrosion applications Alicja Stankiewicz • Irena Szczygieł • Bogdan Szczygie, J Mater Sci (2013) 48:8041–8051 DOI 10.1007/s10853-013-761

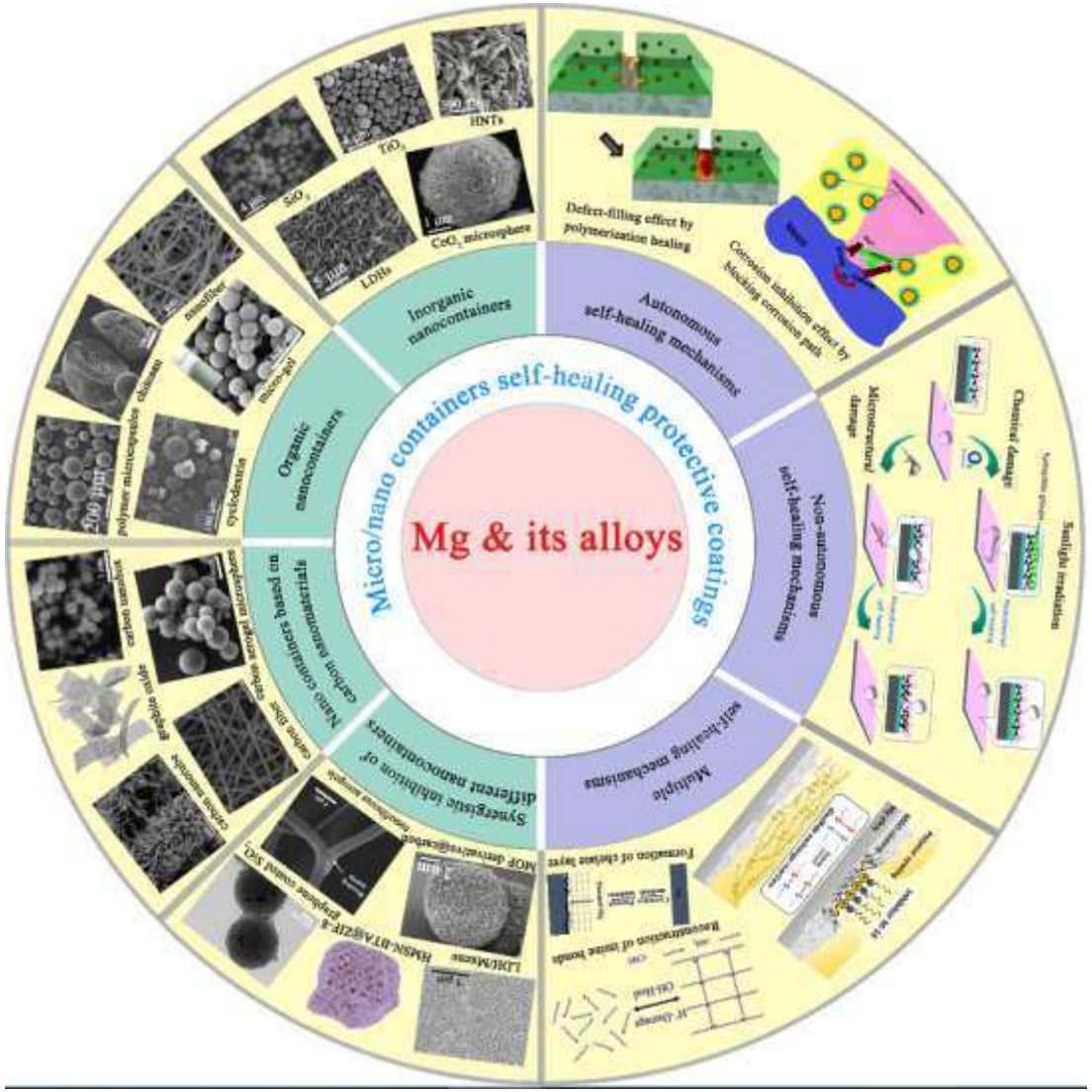
SMART PROTECTIVE COATINGS

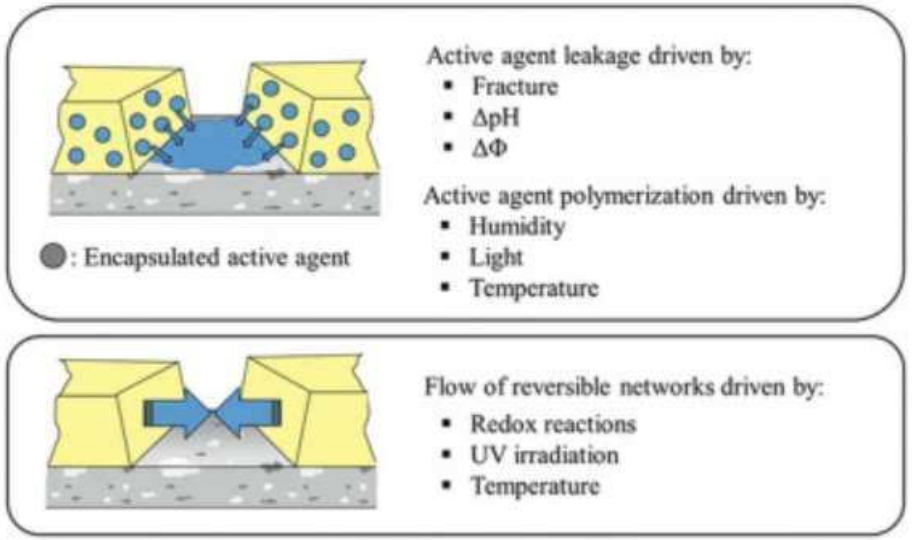


a–d) Schematic illustrations showing different release mechanisms of active payloads from responsive micro- or nanocarriers via degradation of shell carrier (a), degradation of bulk particle (b), swelling of carriers (c), and dissolution or diffusion of ionized payloads (d)

Self-healing coatings in anti-corrosion applications Alicja Stankiewicz • Irena Szczygieł • Bogdan Szczygie, J Mater Sci (2013) 48:8041–8051 DOI 10.1007/s10853-013-761

SMART PROTECTIVE COATINGS





Extrinsic self-healing is achieved by encapsulated active agents.

There are also classifications according to extrinsic (top) and intrinsic healing methods (bottom) as shown in Fig. 1

SMART PROTECTIVE COATINGS

SYNTHESIS OF BINDER

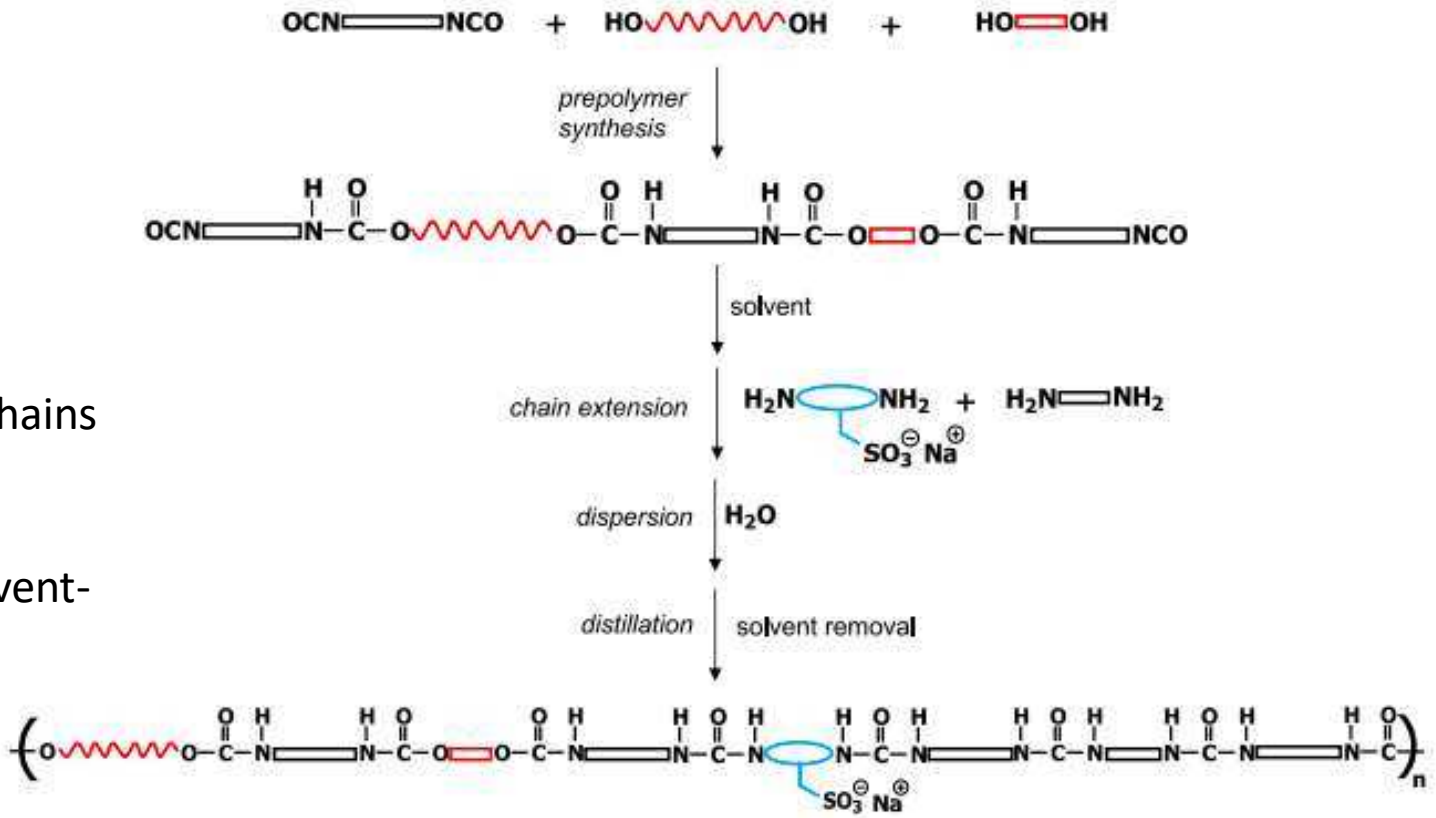
Waterborne Polyurethane Dispersions as Binder:

- Zero/Low Volatile Organic Content (VOC)
- Environmentally Friendly
- User Friendly
- Multicomponent Structure: Tunable Properties
- Colloidal System, High molecular weight WPU chains dispersed in water
- Comparable properties and performance to solvent-borne analogues

SYNTHESIS OF BINDER

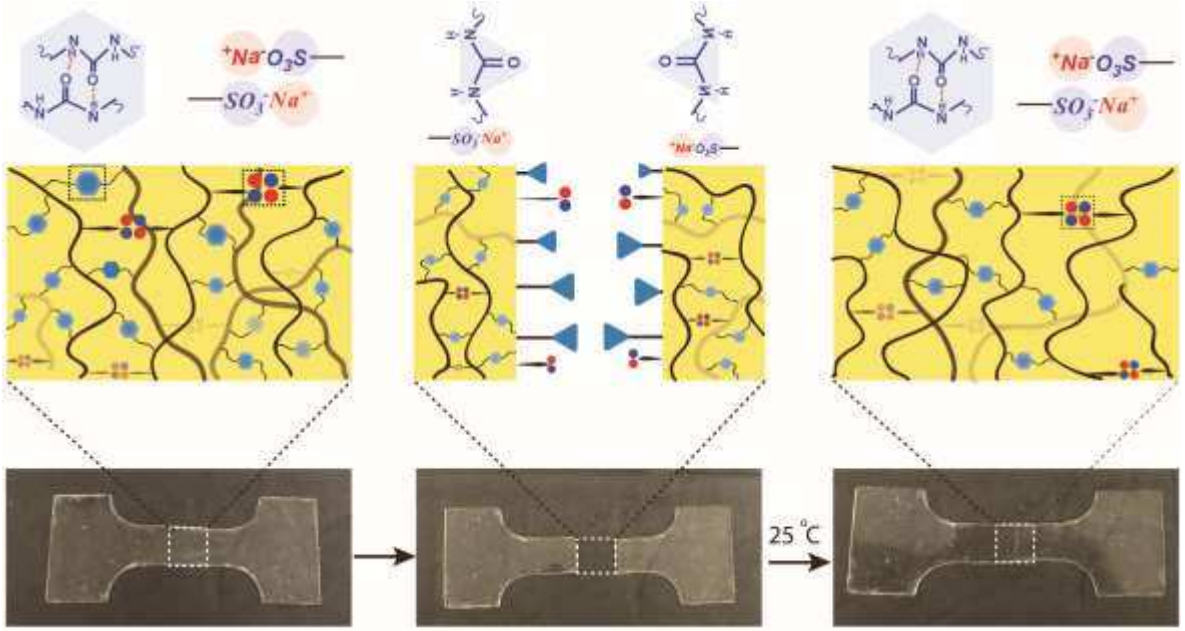
Waterborne Polyurethane Dispersions as Binder:

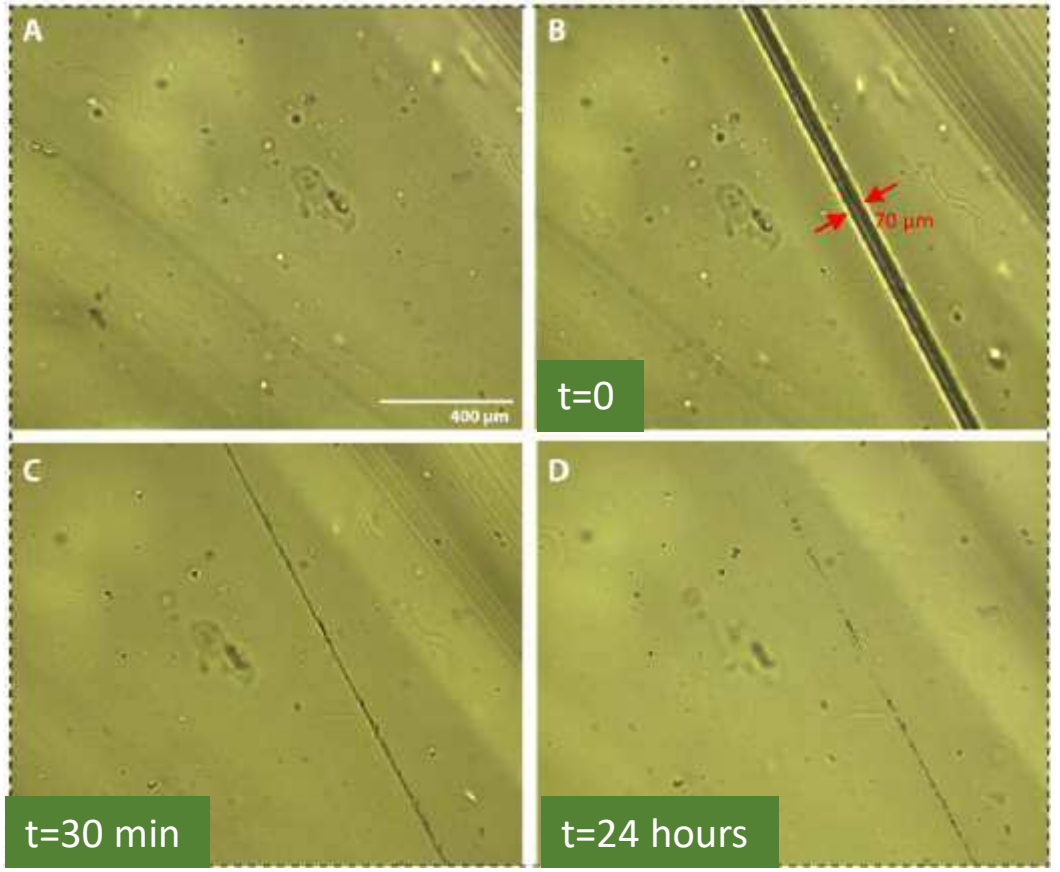
- Zero/Low Volatile Organic Content (VOC)
- Environmentally Friendly
- User Friendly
- Multicomponent Structure: Tunable Properties
- Colloidal System, High molecular weight WPU chains dispersed in water
- Comparable properties and performance to solvent-borne analogues



BINDER PROPERTY

Self Healing Mechanisms:





DESIGN OF COATING

High speed mixers have been used in paint preparations. Dye loading performances with each resin were studied during process development studies. Resins are categorized according to their performance.

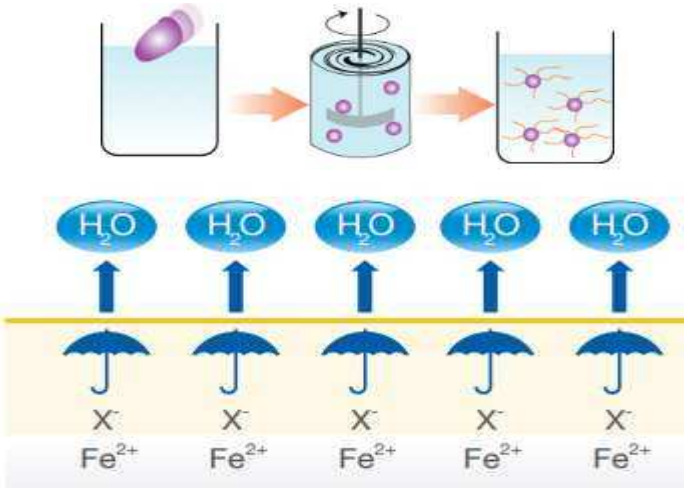


Table 1: Optimization of the formula system used

Raw Materials	FR-1 Std PUD	FR-2 Std PUD	FR-3 SH PUD-01	FR-4 SH PUD-01	FR-5 SH PUD-02	FR-6 SH PUD-02
Std PUD	**70,00**	**70,00**				
SH PUD-01			**70,00**	**70,00**		
SH PUD-02					**70,00**	**70,00**
Additives and Others	3,40	3,40	3,40	3,40	3,40	3,40
TiO2	18,00	18,00	18,00	18,00	18,00	18,00
Anticorrosive Additive	**3,50**	**3,50**	**3,50**	**3,50**	**3,50**	**3,50**
Wax Emuls Hydrfb.	-	**2,00**	-	**2,00**	-	**2,00**
Biocide (in-box preservative)	0,20	0,20	0,20	0,20	0,20	0,20
Film Form. Cosolvent	2,00	2,00	-	-	-	-
Demineralized Water	2,90	0,90	4,70	2,80	4,90	3,00
Total	100,00	100,00	100,00	100,00	100,00	100,00

METHOD AND TESTS

Table 2: Wet paint tests

Test Name	Target Test Results
Determination of Minimum Film Forming Temperature, (ASTM D 2354)	Min 5 °C
Determination of Drying Time (TS 4320 EN ISO 1514, TS 4317, TS 4323)	30 dk/ Hard Dry 1 day
Grinding (ISO 1524, TS 2620 EN ISO 1524)	10 µm
Viscosity (ASTM D 526 ve ASTM D 2196)	7000-10000 cpoise
Density (TS EN ISO 2811-1)	1,16-1,22 g/cm3
Wet and Dry Film Thickness (EN ISO 2808)	300 µm-125 µm
Storage Test(30 day) (TS 39)	<%10 Vis. Chn.
Solid Matter Determination	Min 40

Table 3: Dry film tests

Test Name	Target Test Results
Gloss (ISO 2813, TS EN ISO 2813)	>80
Adesion(TS 4320 EN ISO 1514, TS EN ISO 2409)	GT01 Min
Hardnes(7 gün) (ASTM D 4366 ya da EN ISO 1522)	100
Opacity(ISO 6504-3)	99
Colour YI (ASTM E 313)	Max YI 2,0
Colour WI (ASTM E 313)	Min WI 80
UV Aging Test(ASTM G 154)	Max dE 1,0
Flexibility(TS 4328)	good
Xenon Test (ISO 4892, ISO 11341, ASTM G 155)	Max dE 1,0
Corosion Test	720 h Min

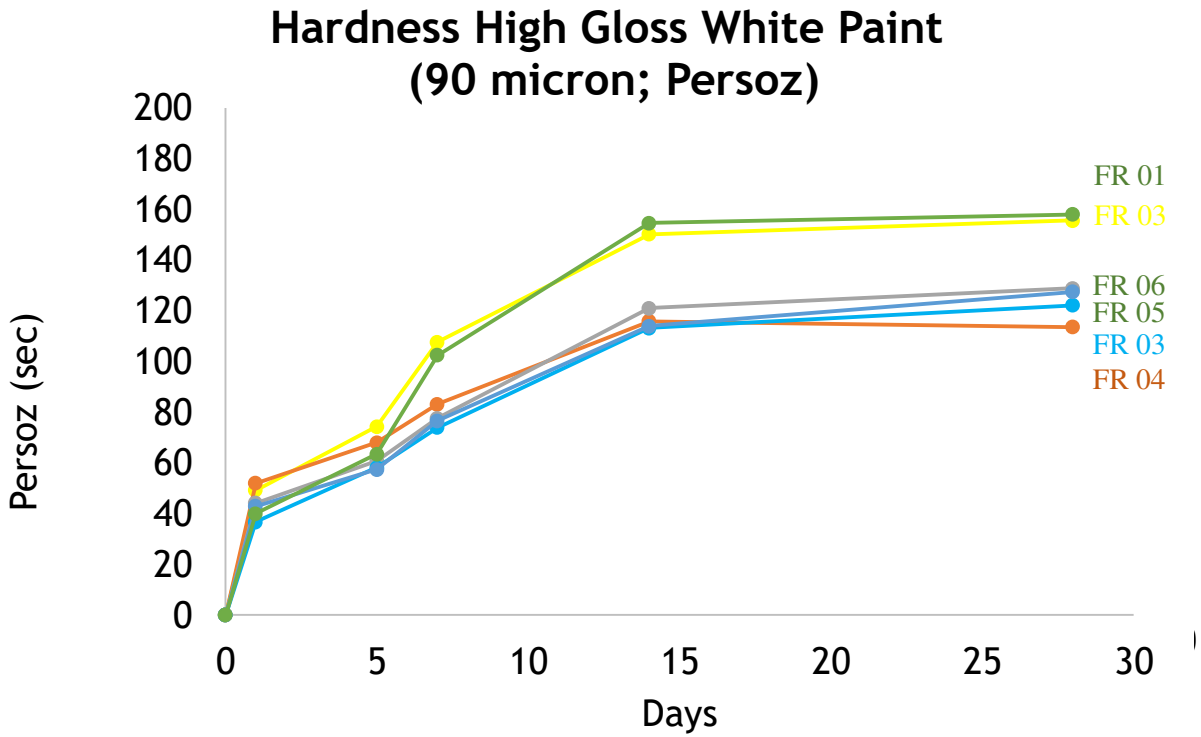
EXPERIMENTAL

Formul Code	Resin Combined	pH	Density (23±2°C) (g/cm3)	Viscosity ICI	Viscosity KU/23±2°C	Viscosity cps/ 23±2°C	Sag Test	Leveling Test
FR1	Std PUD	8,8	1,234	2,61	91,2	7650	good	good
FR2	Std PUD	8,85	1,2115	2,39	91,2	5860	good	good
FR3	SH PUD-01	8,5	1,228	2,46	100	5920	good	excelant
FR4	SH PUD-01	8,83	1,2154	2,14	88,7	5120	good	excelant
FR5	SH PUD-02	9,03	1,2158	2,47	99,4	6120	good	excelant
FR6	SH PUD-02	8,98	1,2153	2,36	96,7	5040	good	excelant

Formul Code	Resin Combined	L	a	b	YI	WI	50°C 1Ay Yaşlandırma Sonrası ΔE	Gloss Test, 20°/60°/85°Gloss
FR1	Std PUD	98,38	-1,2	0,63	0,23	88,5	0,42	92,7 / 99,2 /87,2
FR2	Std PUD	98,04	-0,87	0,56	0,53	89,6	0,38	92,7 /100,4 / 99,7
FR3	SH PUD-01	98,97	-1,07	0,66	0,58	91,4	0,57	86,4 / 88,3 / 98,9
FR4	SH PUD-01	98,32	-0,87	0,8	0,89	88,1	0,3	79,7 /90,1 / 97,2
FR5	SH PUD-02	96,04	-0,96	1,66	1,77	86,6	0,89	61,7 / 87,2 /91,2
FR6	SH PUD-02	98,14	-0,97	0,66	0,58	89,6	0,43	76,3 /91,2 / 98,4

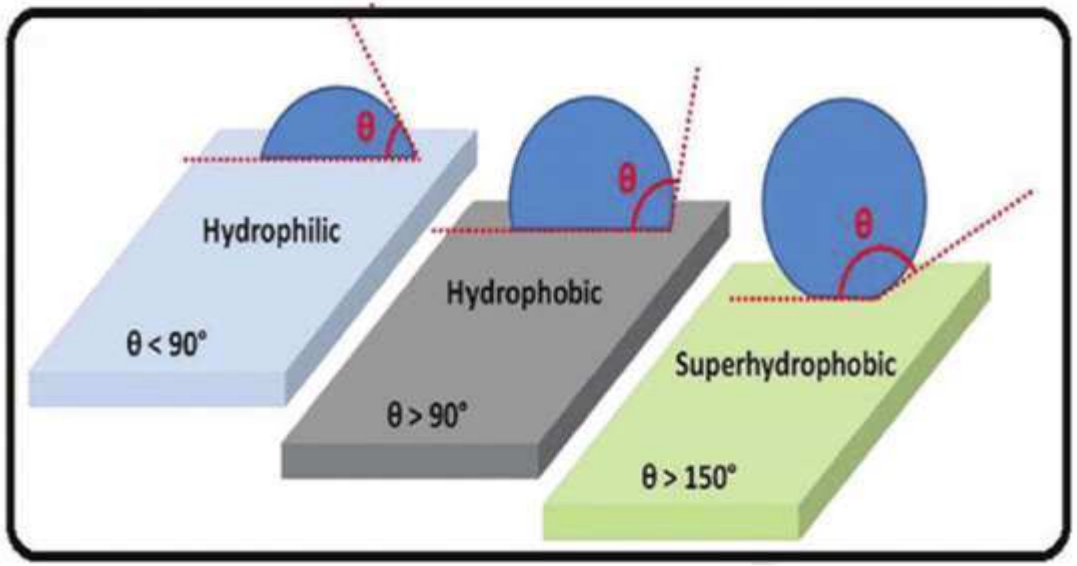
EXPERIMENTAL

Formul Code	Resin Combined	Impact Test		Adhesion Test DTM	Adhesion Test with Primer	720 hr Salt Sprey
FR1	Std PUD	good	60	GT0	GT0	meadyum
FR2	Std PUD	poor	80	GT3	**GT1**	good
FR3	SH PUD-01	good	80	GT2	**GT1**	poor
FR4	SH PUD-01	excelant	**80**	**GT1**	**GT0**	excelant
FR5	SH PUD-02	excelant	**80**	**GT1**	**GT0**	good
FR6	SH PUD-02	excelant	80	GT0	GT0	excelant



EXPERIMENTAL

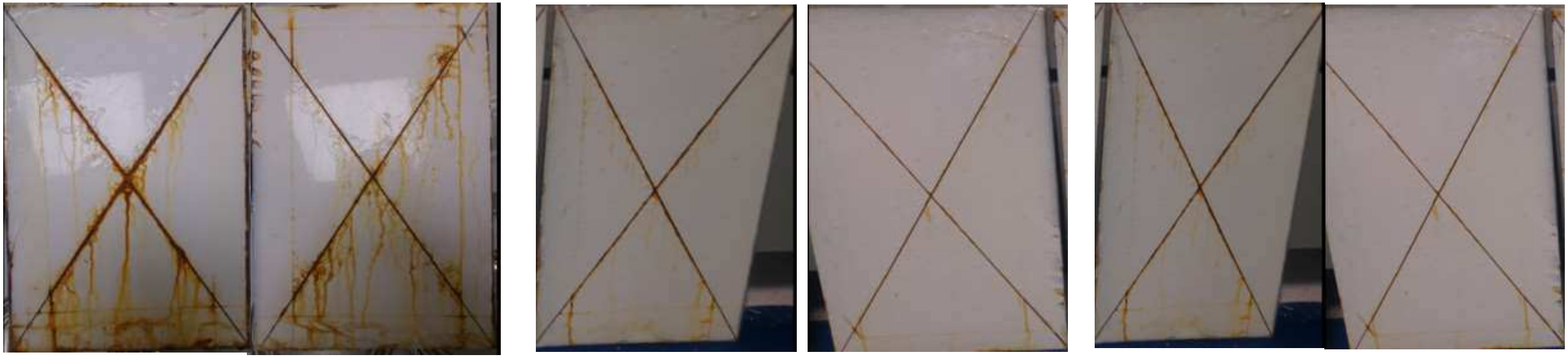
Measure Result	FR-1 Std PUD	FR-2 Std PUD	FR-3 SH PUD-01	FR-4 SH PUD-01	FR-5 SH PUD-02	FR-6 SH PUD-02
1	98	103	96	101	105	110
2	99	99	94	104	109	114
3	93	107	92	105	100	105
4	93	105	93	104	100	105
5	98	109	97	105	105	110
Mean	**97**	**104**	**96**	**104**	**104**	**109**



EXPERIMENTAL

Salt Spray 720 hr test results;

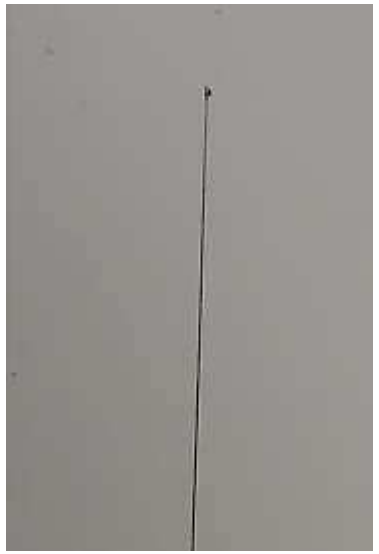
FR-1 Std PUD	FR-2 Std PUD	FR-3 SH PUD-01	FR-4 SH PUD-01	FR-5 SH PUD-02	FR-6 SH PUD-02



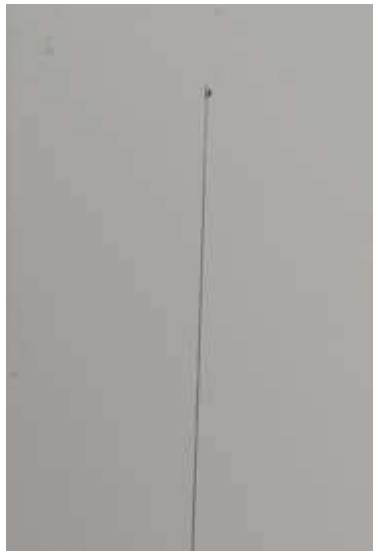
EXPERIMENTAL

24 Hour healing test results for sample **FR 06 with SH PUD2**

Initial

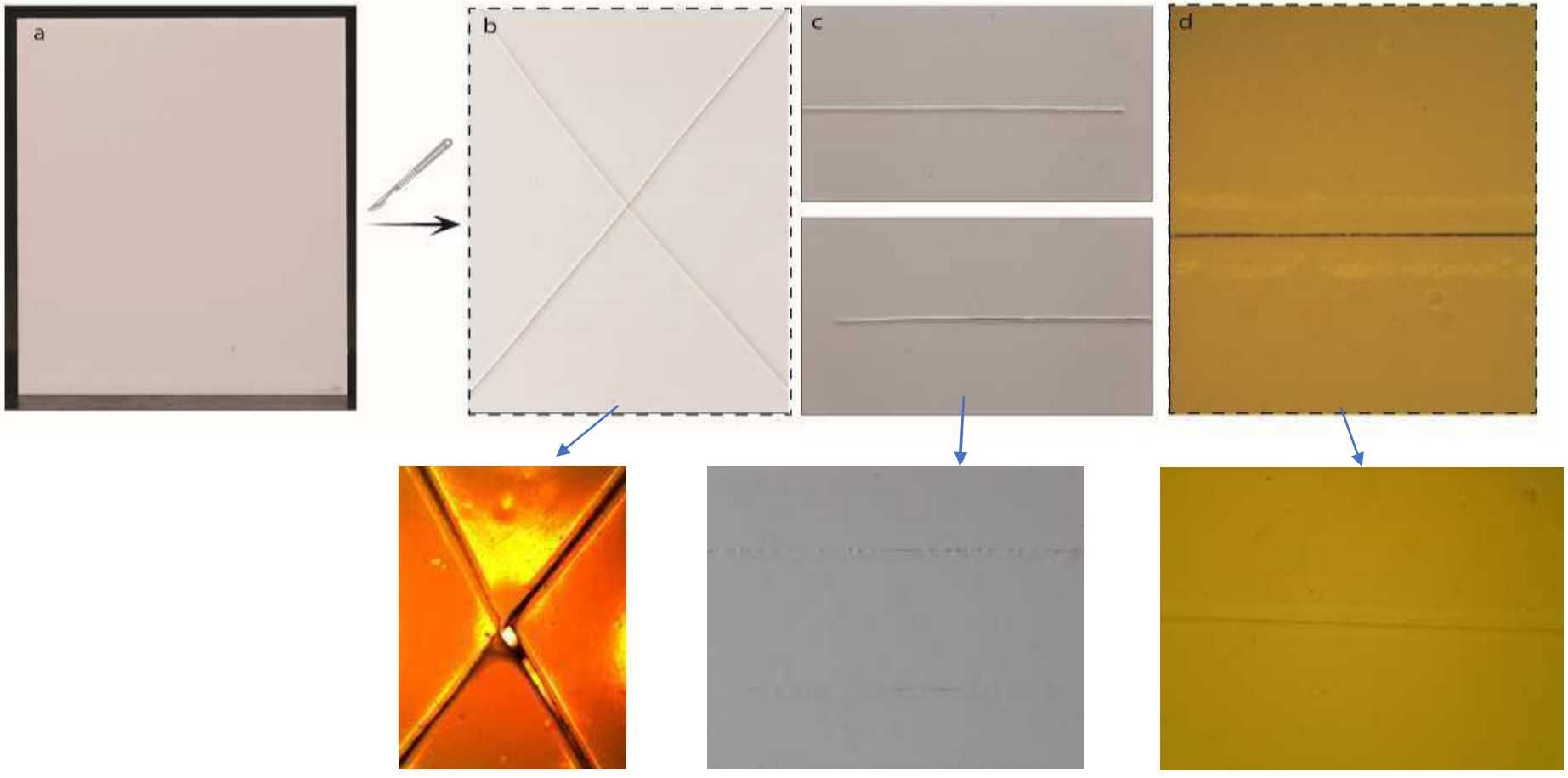


1 Hour Self-Healing



24 Hour Self-Healing

PAINT SELF-HEALING PROPERTY



1 Hour Self-Healing

1 Hour Self-Healing

1 Hour Self-Healing

CONCLUSION

BINDER

- Zero/Low Volatile Organic Content (VOC) Binder synthesized with lov VOC
  - Environmentally Friendly
  - User Friendly
- Self-healing feature was observed
- Multicomponent Structure: Tunable Properties
- Colloidal System, High molecular weight WPU chains dispersed in water
- Comparable properties and performance to solvent-borne analogues

COATING

- Anticorrosive Water Based PU Self- healing Coating is improved with Low VOC Product <50g/L
  - Environmentally Friendly
  - User Friendly 1K S-H PUD Waterborne Anticorrosive Coating
- Self-healing feature was observed
- Anti-Corrosive Properties; It was observed that SH PUDs were better than the Std PU product for 720 hours.

Referances

1. Kianfar M, Mohajer S, Dorraji MSS. Waterborne Polyurethanes for Self-Healing Applications. Eco-Friendly Waterborne Polyurethanes . 2022 Jan 24.
2. Wang S, Urban MW. Self-healing polymers .Vol. 5, Nature Reviews Materials. Nature Research; 2020. p. 562–83.
3. Cho SH, White SR, Braun P V. Self-Healing Polymer Coatings. Advanced Materials . 2009 Feb 9 ;21(6):645–9.
4. Mater J, Chem B, Wang Z, Lu X, Sun S, Yu C, et al. Preparation, characterization and properties of intrinsic self-healing lastomers. 2019.
5. Willocq B, Odent J, Dubois P, Raquez JM. Advances in intrinsic self-healing polyurethanes and related composites. RSC Adv. 2020 Apr 5;10(23):13766–82.
6. https://www.sciencedirect.com/science/article/abs/pii/S0167732217351711#preview-section-abstract
7. Potential use of smart coatings for corrosion protection of metals and alloys: A review Author links open overlay panel,
8. Corrosion-Responsive Self-Healing Coatings September 2023 Advanced Materials 35(47):e2300101 DOI:10.1002/adma.202300101
9. Journal of Magnesium and Alloys Volume 11, Issue 7, July 2023, Pages 2230-2259 “Smart” micro/nano container-based self-healing coatings on magnesium alloys: A review
10. https://www.sciencedirect.com/science/article/abs/pii/S0167732217351711#preview-section-abstract
11. Potential use of smart coatings for corrosion protection of metals and alloys: A review Author links open overlay panel,

Polisan HOME COSMETICS

Sabancı Üniversitesi

THANK YOU...

BOSAD BOYA SANAYİCİLERİ DERNEĞİ THE ASSOCIATION OF PAINT INDUSTRY 2003-2023 20

paintistanbul TURKCOAT CONGRESS

ChemMedia by Artkim Group