

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

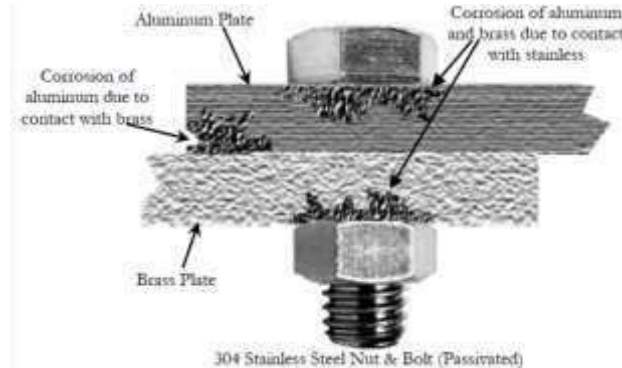
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Solvent Based Industrial & Decorative Coatings

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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.

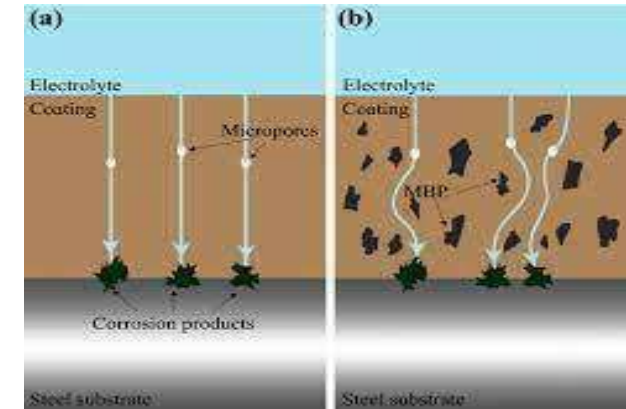
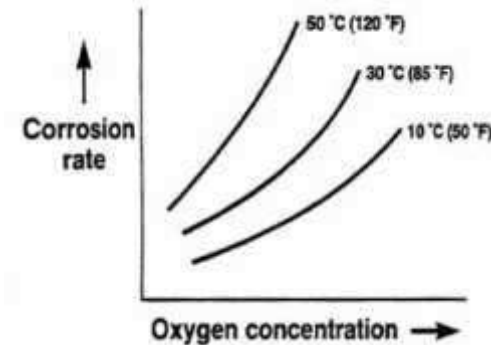


Corrosion is the loss of materials(metal and alloys) or its useful properties, by chemical or electrochemical interaction with its environment.

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 presence of

- Impurities
- 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)

Hence, smart corrosion protection based on stimuli responsive 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.

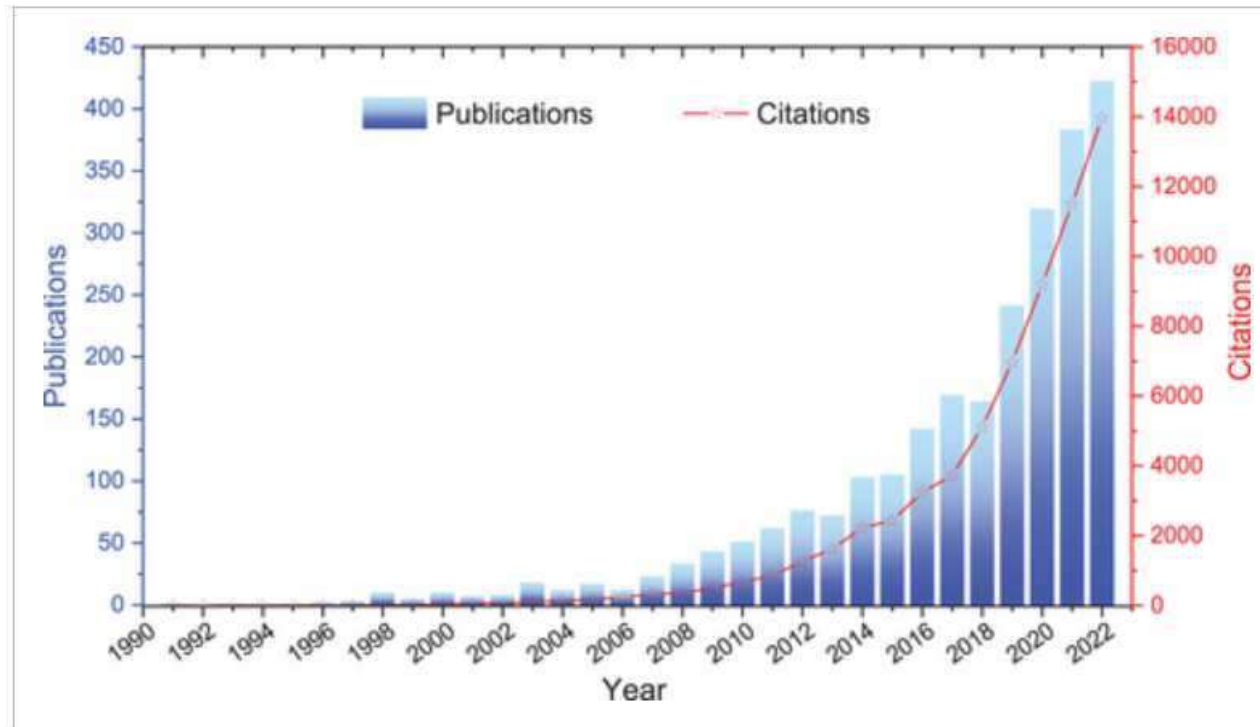
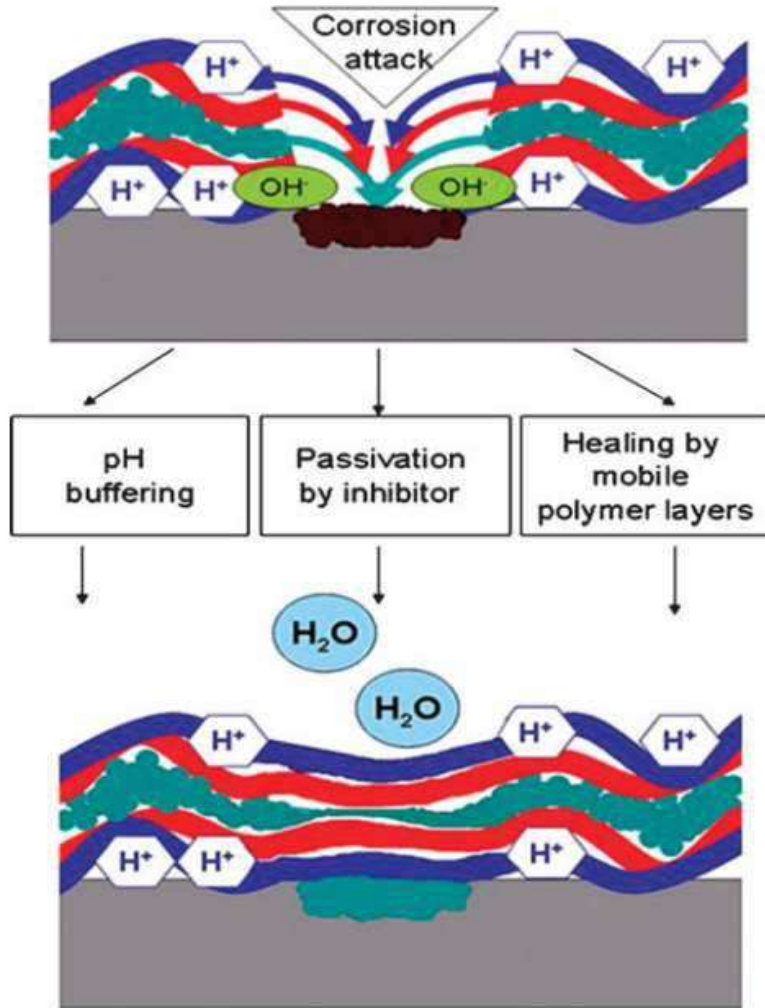
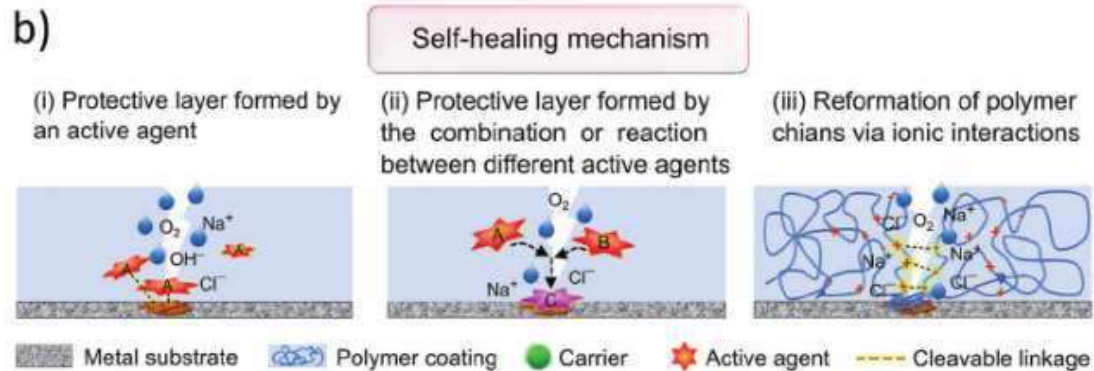


Figure1 Publications per years on smart self-healing coatings for corrosion protection



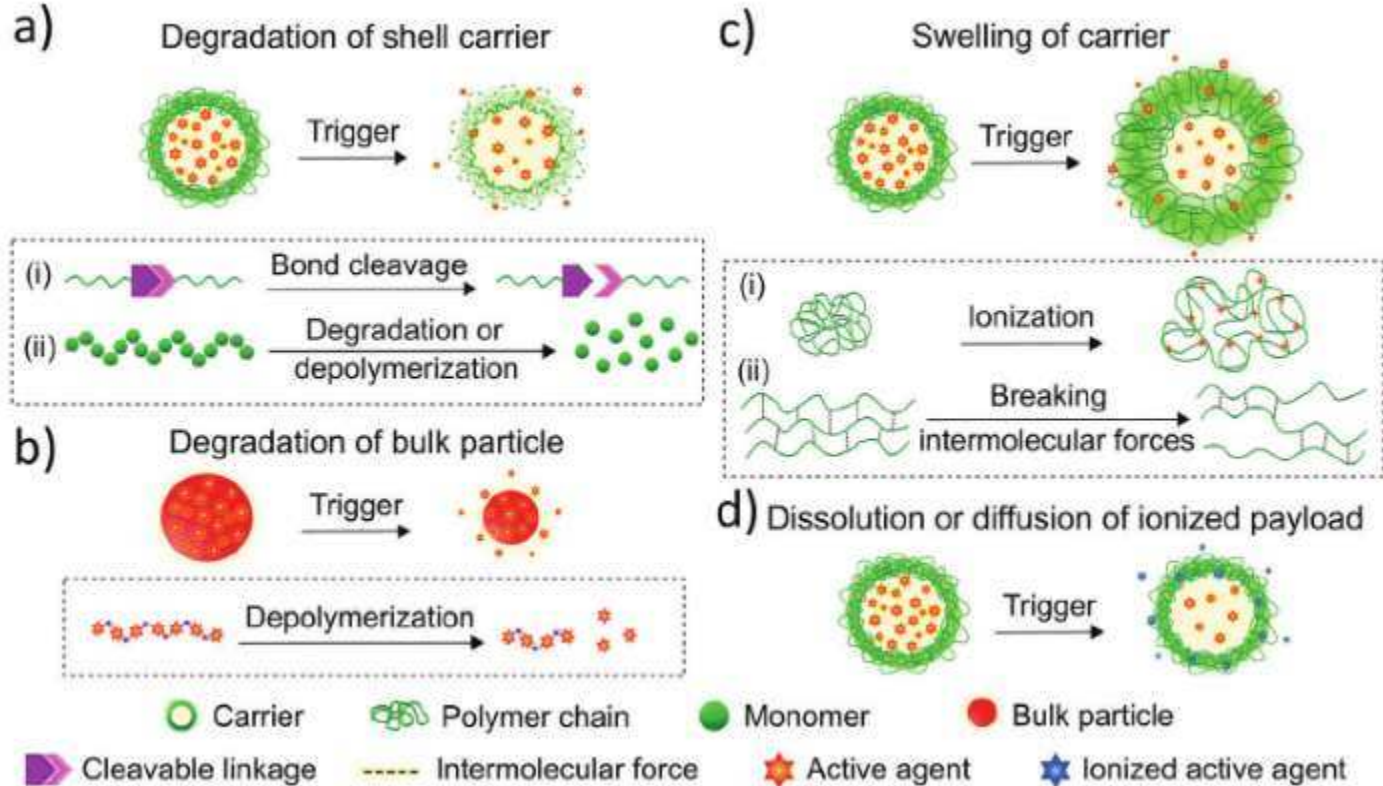
- The addition of corrosion inhibitors directly to coatings, which is one of the possibilities of protecting a metallic substrate against the action of a corroding medium.
- The encapsulation of corrosion inhibitors and the introduction of the capsules into the matrix of the coating are considered to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

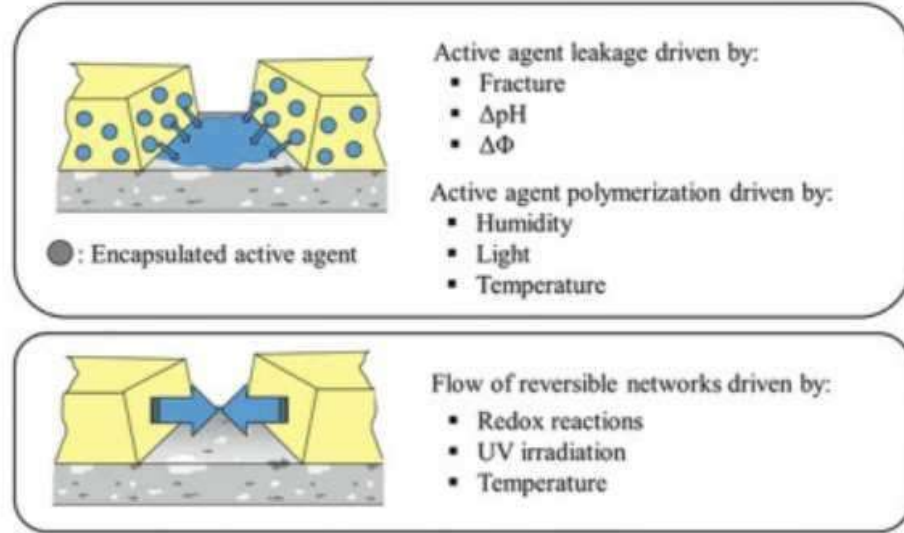
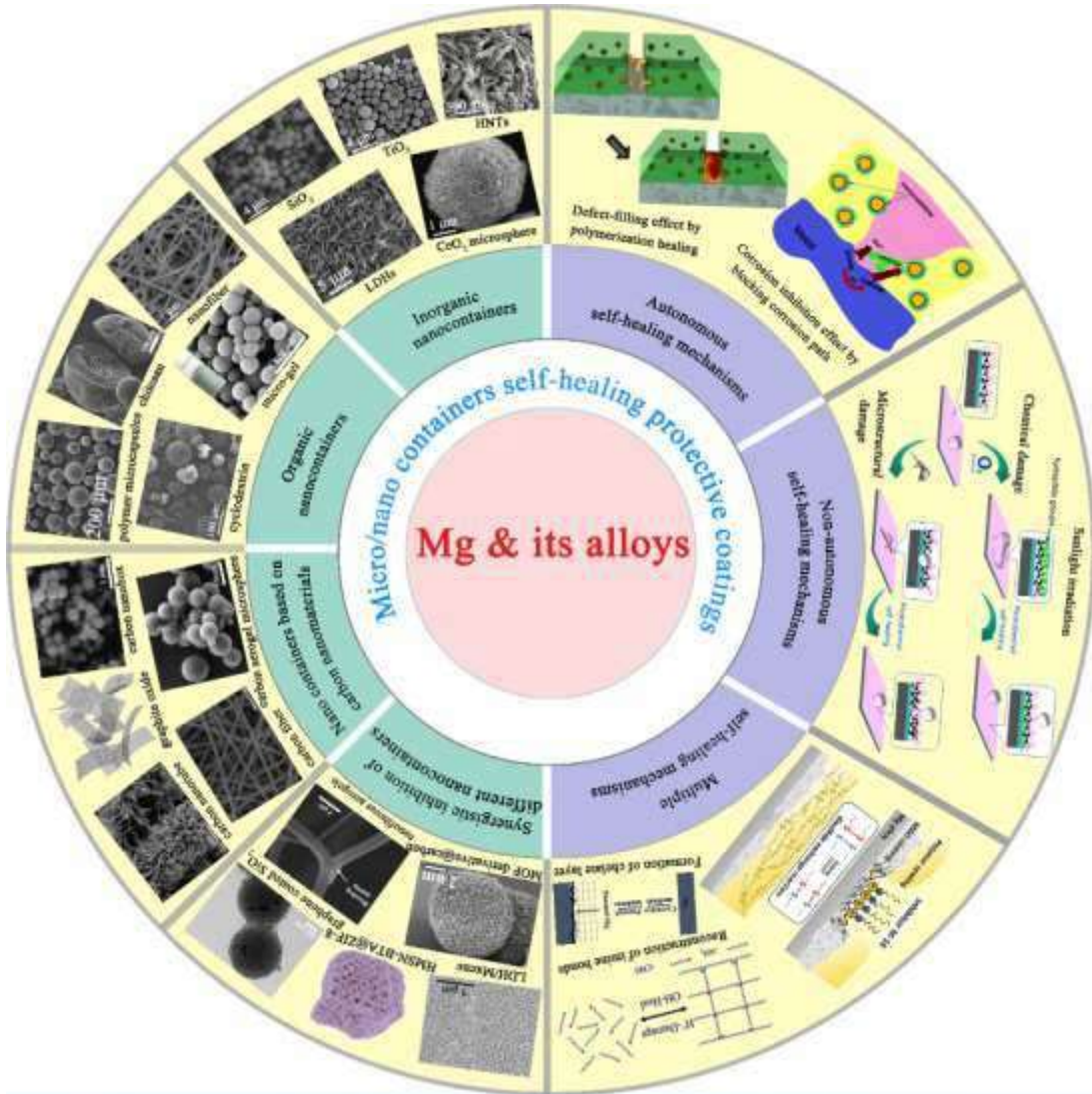


- a) Schematic illustrations for extrinsic (i) and intrinsic (ii) responsive self-healing materials for anticorrosion and
- b) self-healing mechanism of coatings for anticorrosion relying on the formation of protective layers, which are produced by an active agent (i), by the combination/reaction between 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 Szczygieł, *J Mater Sci* (2013) 48:8041–8051 DOI 10.1007/s10853-013-761



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)



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

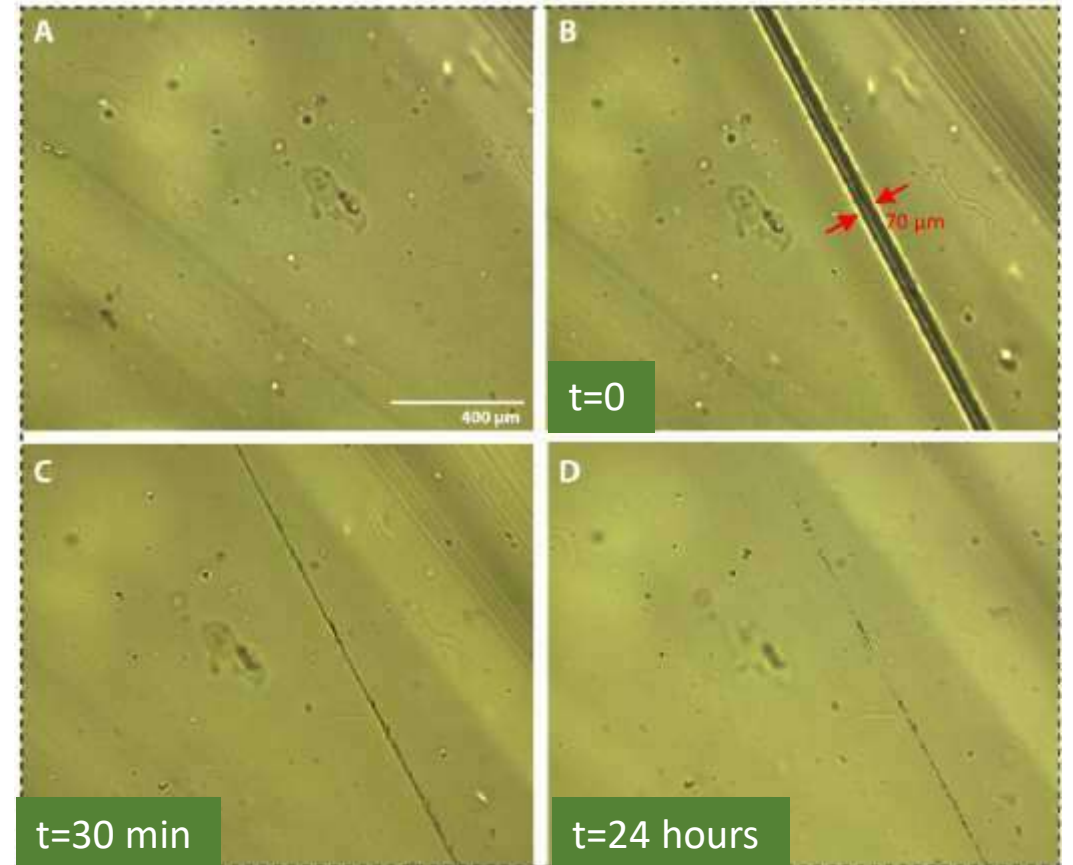
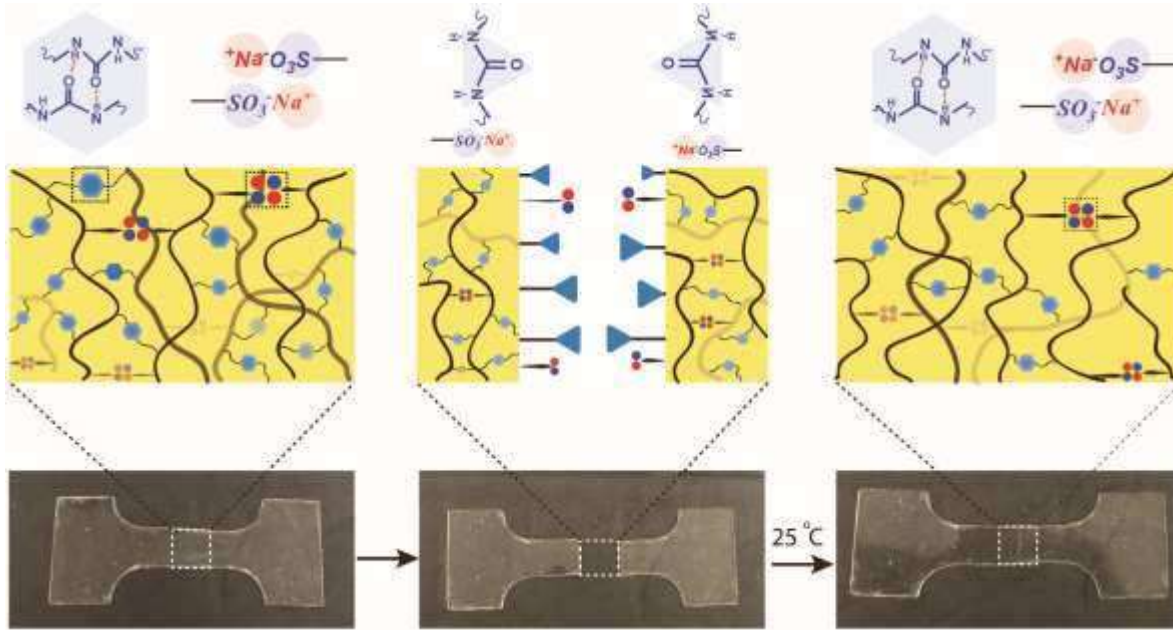


Waterborne Polyurethane Dispersions as Binder:

- 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



Self Healing Mechanisms:



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

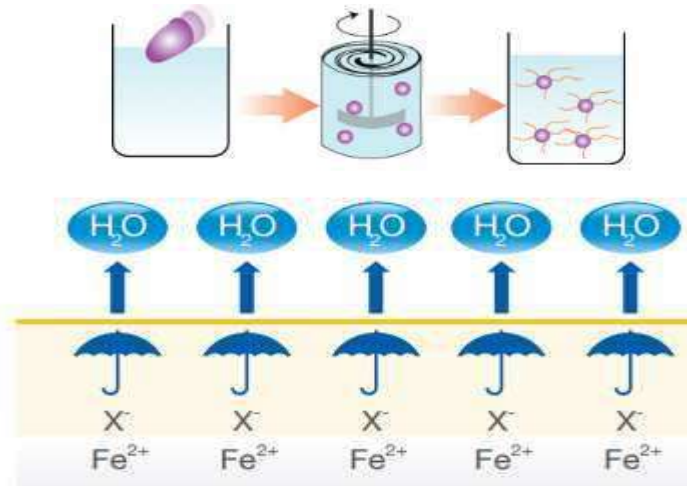


Table 2: Wet paint tests

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/cm ³
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

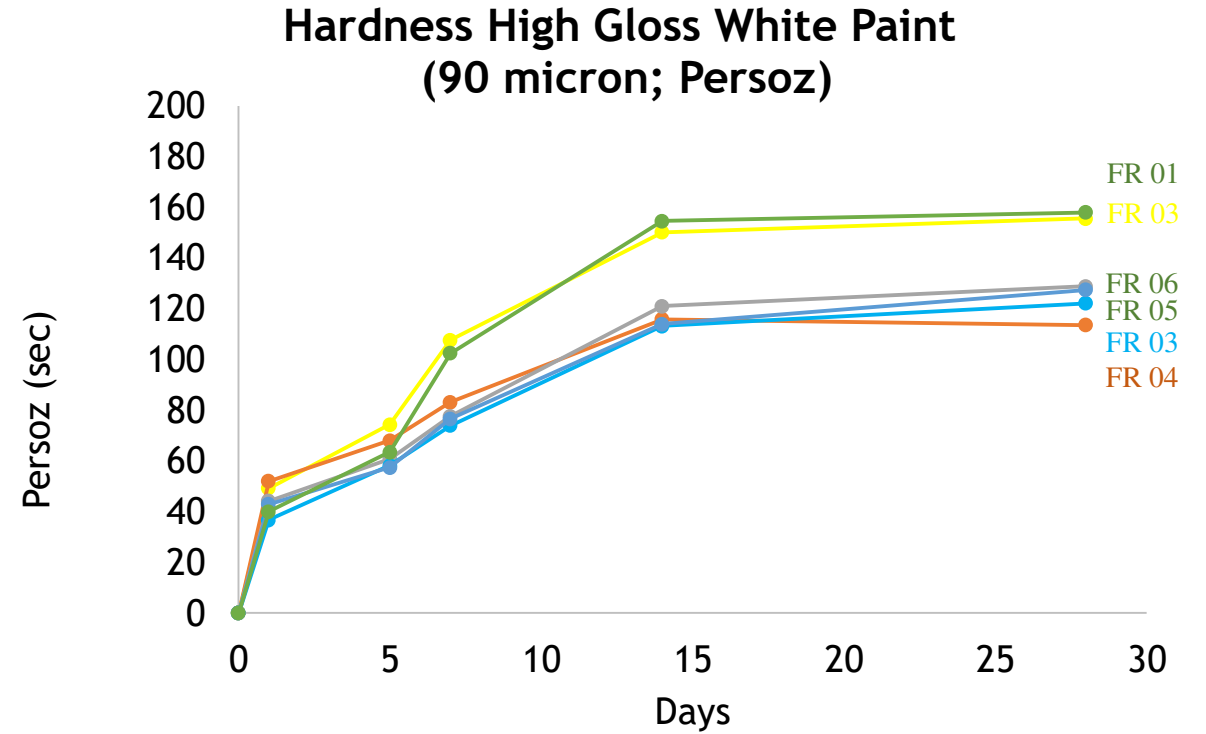
Table 3: Dry film tests

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

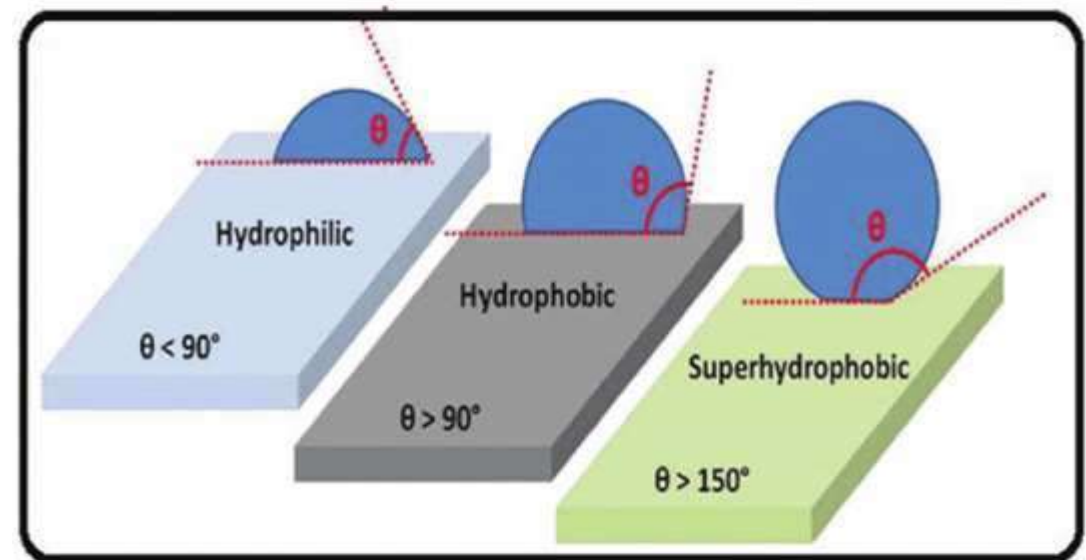
Formul Code	Resin Combined	pH	Density (23±2°C) (g/cm3)	Viscosity ICI	Viscosity KU/23±2°C	Viscosity cps/ 23±2°C	Sag Test	Leveling Test
FR1	Std PUD	8,8	1,234	2,61	91,2	7650	good	good
FR2	Std PUD	8,85	1,2115	2,39	91,2	5860	good	good
FR3	SH PUD-01	8,5	1,228	2,46	100	5920	good	excelant
FR4	SH PUD-01	8,83	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

Formul Code	Resin Combined	Impact Test	Adhesion Test DTM	Adhesion Test with Primer	720 hr Salt Sprey	
FR1	Std PUD	good	60	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



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



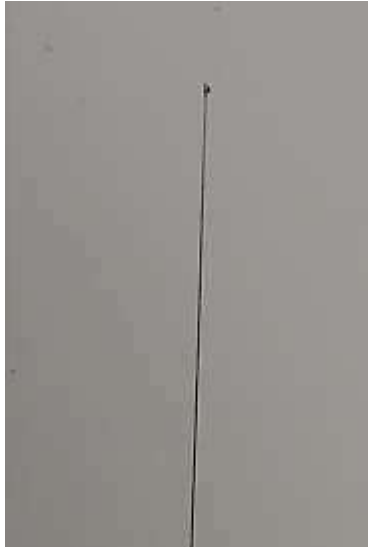
Salt Spray 720 hr test results;

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



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

Initial



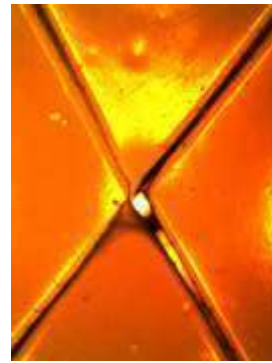
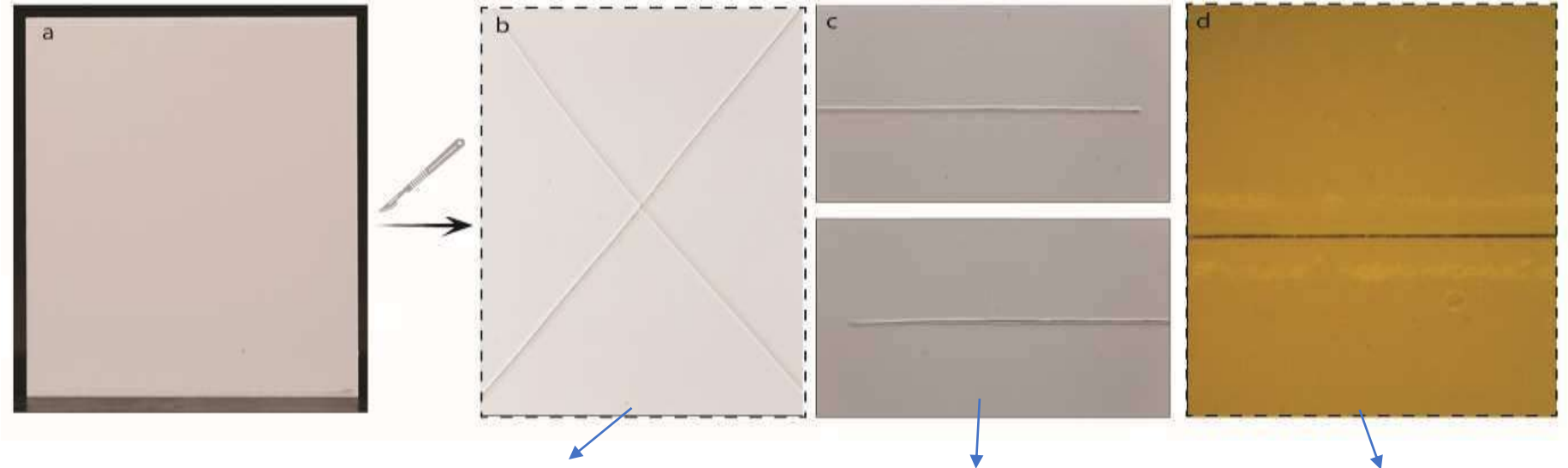
1 Hour Self-Healing



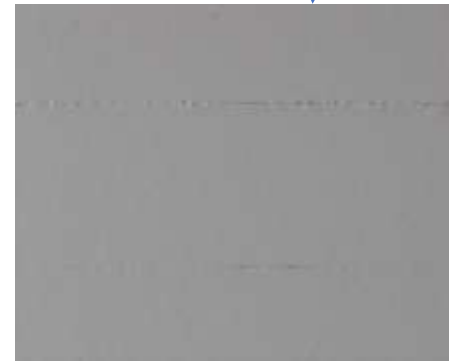
24 Hour Self-Healing



PAINT SELF-HEALING PROPERTY



1 Hour Self-Healing



1 Hour Self-Healing



1 Hour Self-Healing

BINDER

- Zero/Low Volatile Organic Content (VOC) Binder synthesized with low 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.

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THANK YOU...