paintistanbul TURKCOAT CONGRESS

Effects of CeO_2 Nano and Micro Particles on Anti-Bacterial and Physical Properties of Acrylic Resin Water-Based Paints

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December 2023

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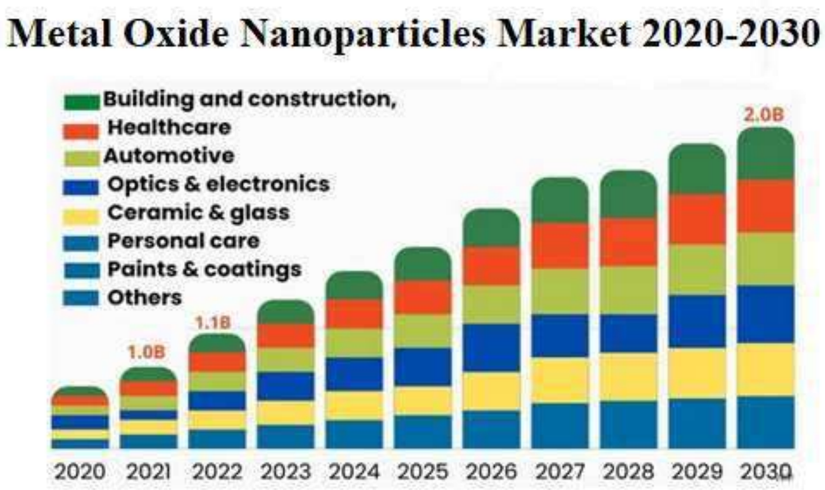
Outline

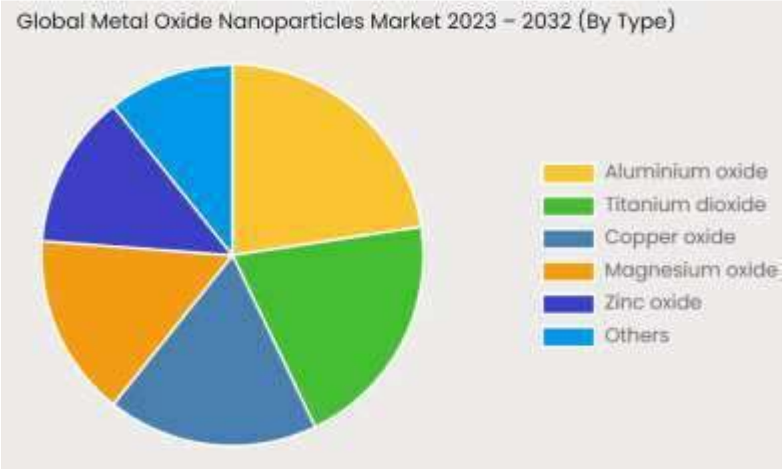
- **NanoMetaloxides and Their Usage in Paint**
- **Ceriumoxide and Nanoceria in Paint**
- **Nanoceria Dispersed Acrylic Resin Based Paint**
  - Formulation and Physical Test Results
  - Performance Tests
  - Antibacterial Activity

NANO METALOXIDES IN PAINTS

There are many studies have shown that nanometaloxide particles introduced into paints to improve their features.

Metal salts are used for synthesis, reducing agents ($NaBH_4$, sodium citrate, ascorbic acid) and capping agents (polymers, citrate, thiol) in chemical reduction methods.
In green synthesis of NMPs pure biomaterials or extracts related to plants, bacteria, fungi, algae, lichens, yeasts and viruses are used as reducing and caping agents. [1]

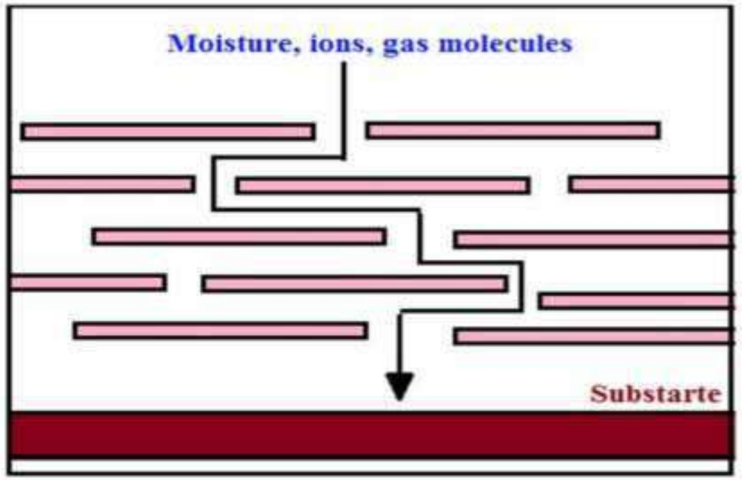




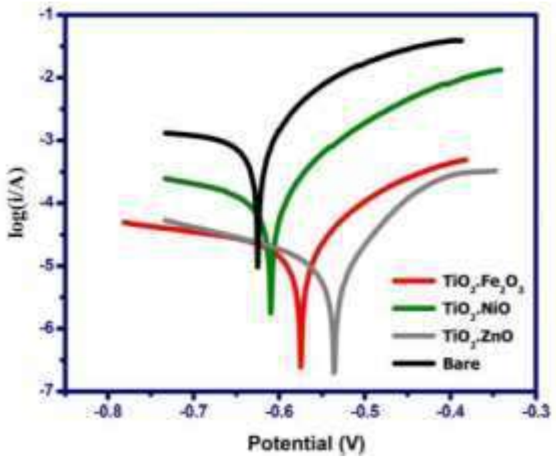
[2] https://www.custommarketinsights.com/report/metal-oxide-nanoparticles-market/

- Alkyd-clay nanocomposites improved the anticorrosion and mechanical performance of coatings [3].

Coated panels after 500 h salt spray chamber [3]



Corrosion resistance mechanism of alkyd-clay nanocomposites [3]

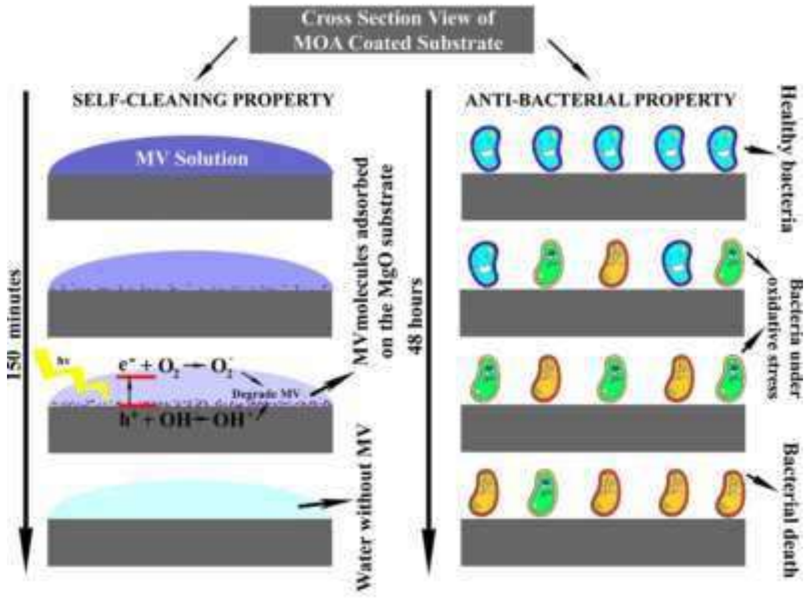


Tafel plots for bare and CTF, CTZ and CTN A36 steel plates[4]

EN-0 : %0 O-MMT +alkyd+ pigments+ extenders
EN-1 : %1 O-MMT +alkyd+ pigments+ extenders
EN-3 : %3 O-MMT +alkyd+ pigments+ extenders

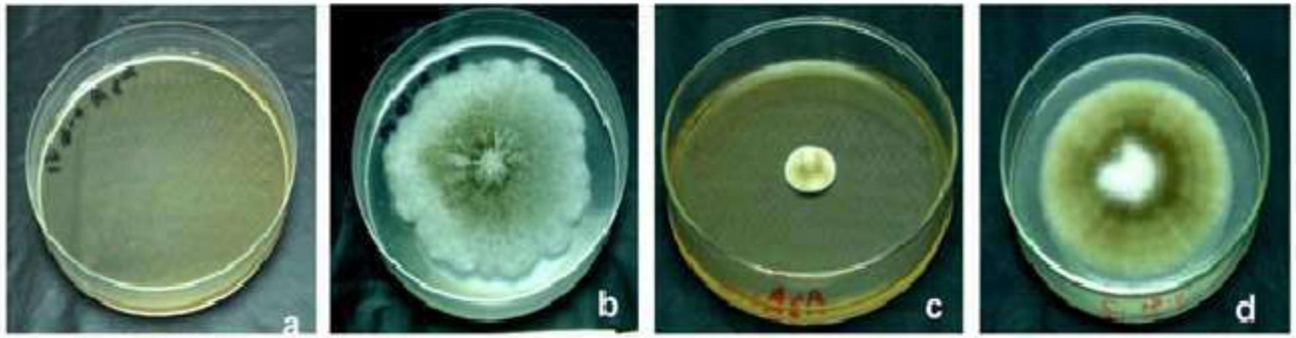
- The specimens coated with alkyd resin containing mixed nano-metal oxides (TiO_2 center Fe_2O_3/ZnO/NiO) exhibited higher corrosion protection efficiencies [4].

- MgO nanoparticles dispersed in alkyd coatings possessed self-cleaning behavior, and degraded methyl violet dye when exposed to sunlight [5].



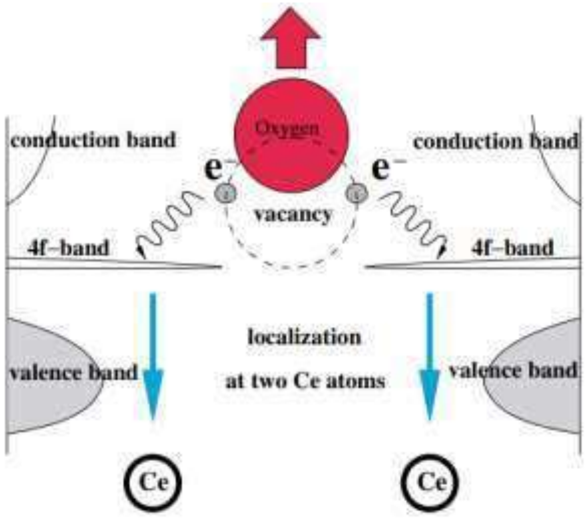
Photocatalytic and antibacterial behavior of MgO [5]

- Incorporation of silver, copper and zinc oxide nanoparticles in indoor waterborne paints were evaluated and it is seen that they inhibit the growth of C. Globosum and A. Alternata. [6]



C. Globosum and A. Alternata (c and d) in solid media with AgA (a and c) and without NP (b and d) [6]

CERIUM OXIDE



The process of oxygen-vacancy formation in ceria [7]

1) $Katalist + h\nu \rightarrow e^- + h^+$

2) $(H_2O \leftrightarrow H^+ + OH^-) + h^+ \rightarrow H^+ + OH^\bullet$

3) $O_{2(g)} + e^- \rightarrow O_2^{\bullet -}$

4) $O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet$

5) $2\ HO_2^\bullet \rightarrow H_2O_2 + O_2$

6) $H2O2 + e^- \rightarrow OH^- + OH^\bullet$

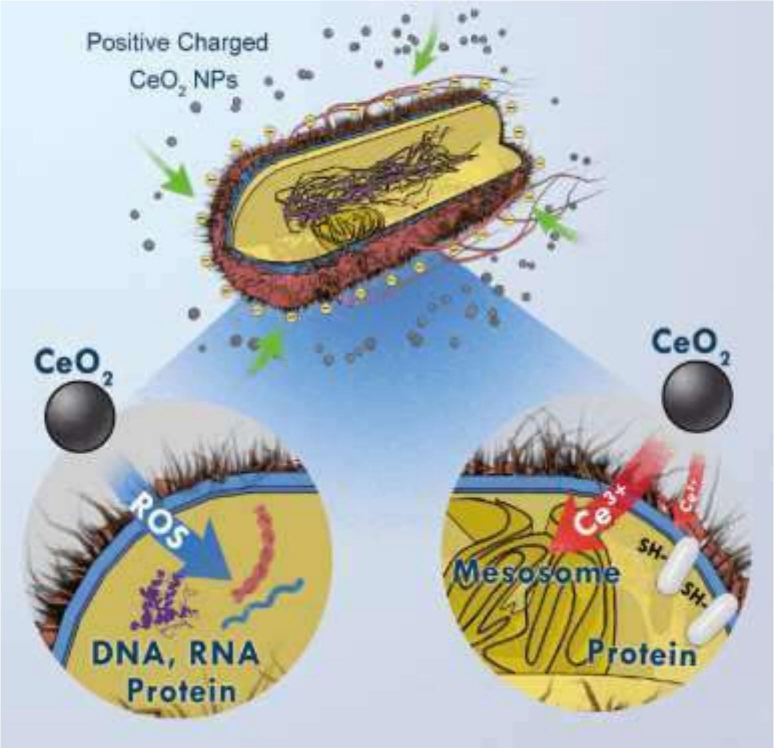
7) $R + h^+ \rightarrow R^{+o}$

8) $R + OH^\bullet \rightarrow R'^\bullet + H_2O$

Cerium oxide is a metal oxide which is used as a catalyst, brightening agent, atioxidant and UV absorber in many fields, from physics to chemistry, from biology to materials science, with the ability to transform between Ce^{+3} and Ce^{+4} oxidation steps quickly and easily.

It is one of the most abundant of rare-earth metals found in Eart's crust (66.5 ppm) [8]. Some of Cerium minerals are bastnasite (Ce,La)(CO_3)F and monazite (Ce, La, Nd, Th)(PO_4) [9].
Cerium oxide or nanoceria have relatively lower or even no toxicity to mammalian cells [10].

Antibacterial Mechanisms of CeO2



Toxicity of CeO_2 NPs against bacterial pathogens [7]

1- NPs generate ROS. ROS contain unpaired valence electrons which induce severe damage to cellss including DNA and RNA and cause to oxidations of lipids and proteins and enzyme deactivation.

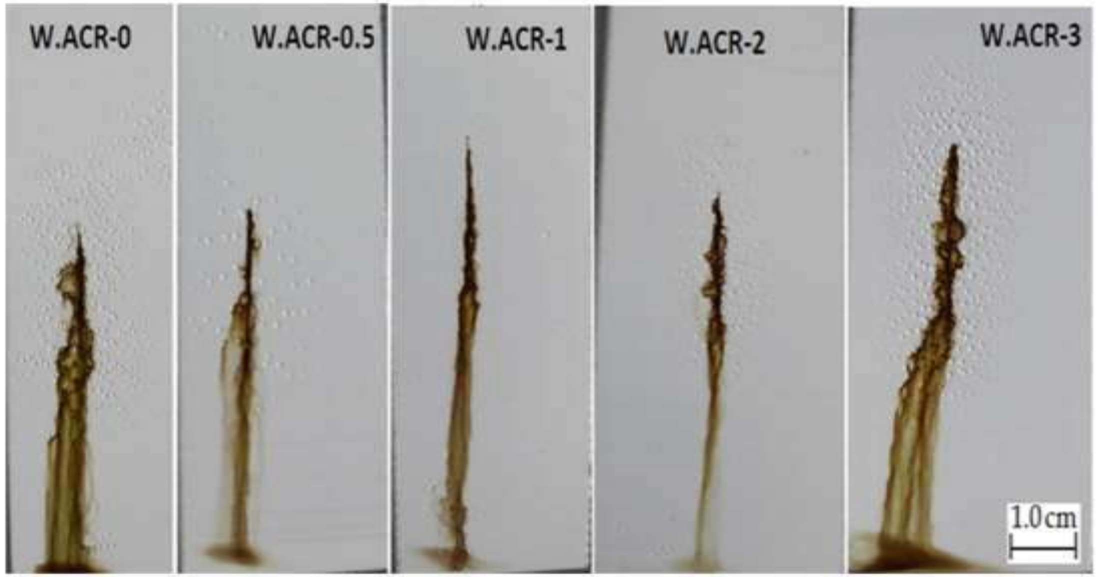
2-NPs adsorb ontosurface of bacterial membranes, they bind with mesosome and interfere with the cellular respiration, DNA replications, cell division and inrease the surface are of bacterial membrans. NPs react with the Thiol groups (-SH) in the proteins on the bacterial membranes. These proteins extrude through the cell membrane and have the function of nutrients transportation. This tresults in decreasing permeability of membranes and death of cells.

3-Irregularr shapes or rough surfaces of NPs gives physical damage to the bacteria [7].

CERIUM OXIDE IN PAINTS

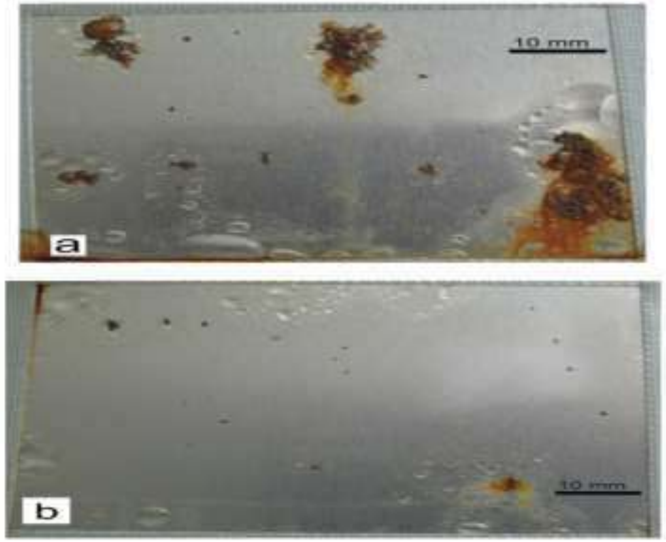
- The main technological applications of cerium-based oxide coatings are reviewed by Castano et al. [11]. They are very good in catalysis and corrosion prevention.

- Apart from alkyd coatings, enhanced corrosion protection efficiency has been reported from the incorporation of nanoceria into the primer layer of waterborne acrylic paint [12].



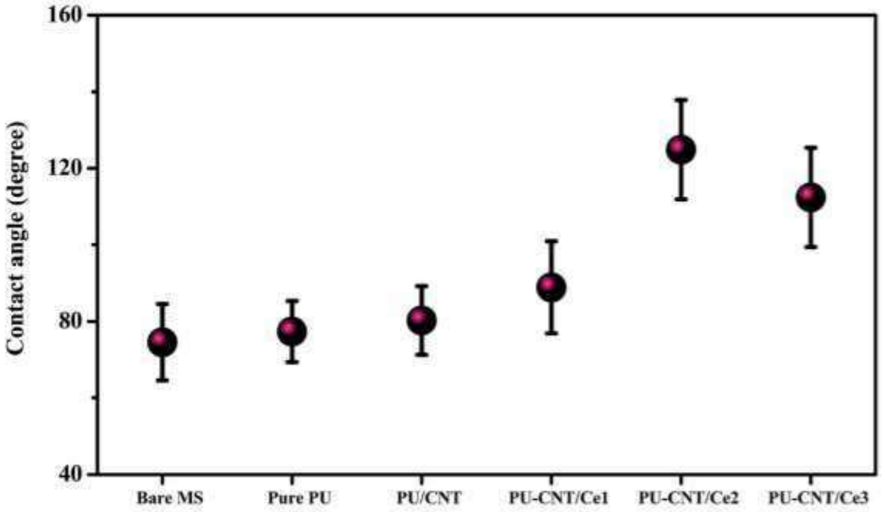
Surface of the S Blank (a) and S Ceria (b) panels after 168 h of exposure on salt spray chamber [12]

- The anticorrosive properties of an alkyd coating loaded with polyaniline and cerium oxide nanoparticles were presented in another paper [13].



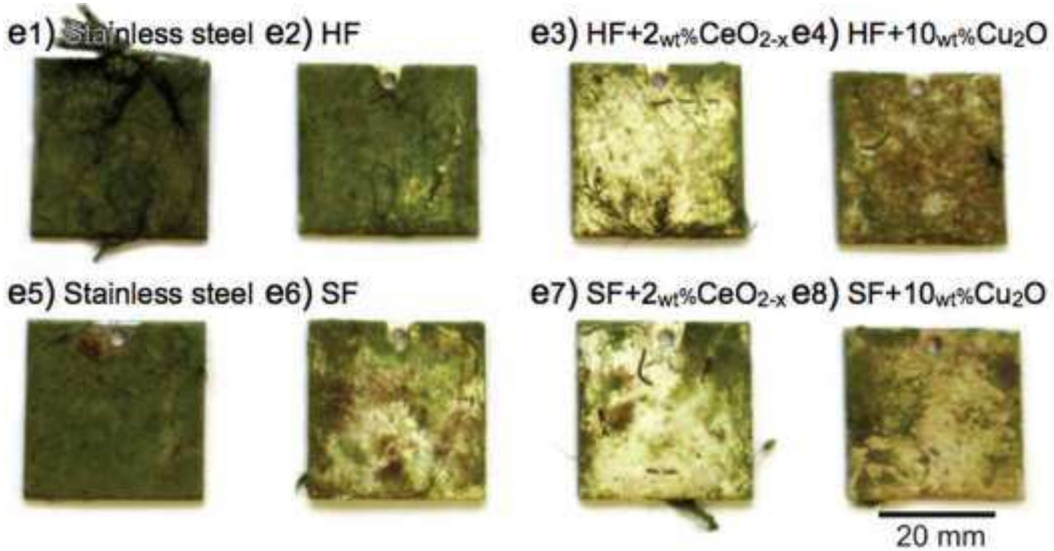
Surface of the S Blank (a) and S Ceria (b) panels after 168 h of exposure on salt spray chamber [13]

- The addition of nano-cerium oxide together with carbon nanotubes into polyurethane coatings improved the corrosion resistance of the coating. The water contact angle increased linearly with increasing CNT nanocomposite amounts in the coatings to further support the enhanced corrosion performance on the MS surface [14].



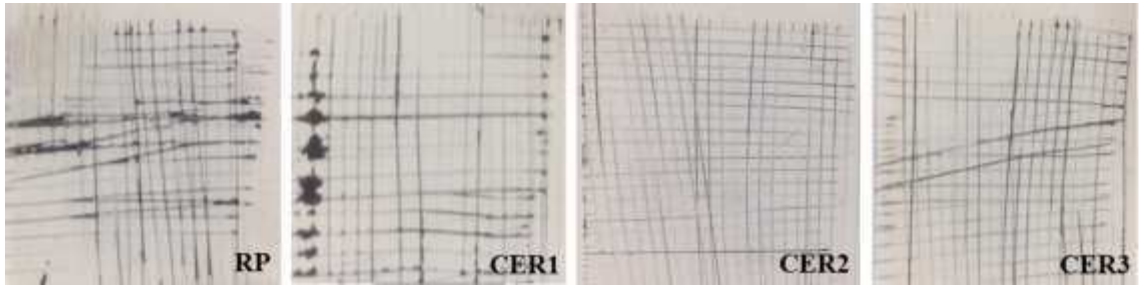
Contact angle results of the uncoated and coated MS substrates [14]

- In one study, ceria has been offered as antifouling biocide with replcement cuprous oxide [15].



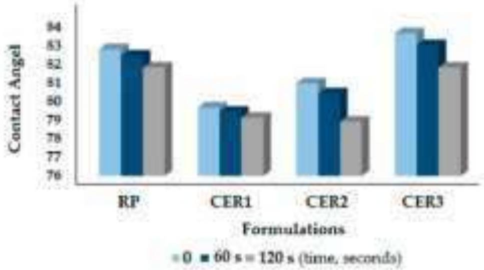
e1, e5 stainless stell , e2, e6 HF, SF w,thout biocide, e3, e7 HF and SF containing %2 CeO_{2-x} nanorods, e4 and e8 HF and SF containing %10 wt of CuO_2 [15]

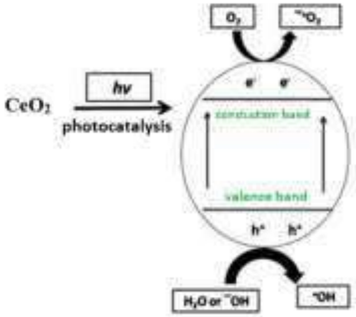
- In our previous study it has been proved that the use of macro and nano cerium oxide gives paints resistance against corrosion, UV-aging and provides self cleaning effect besides physical advantages such as hardness, adherence and impact resistance. [16]



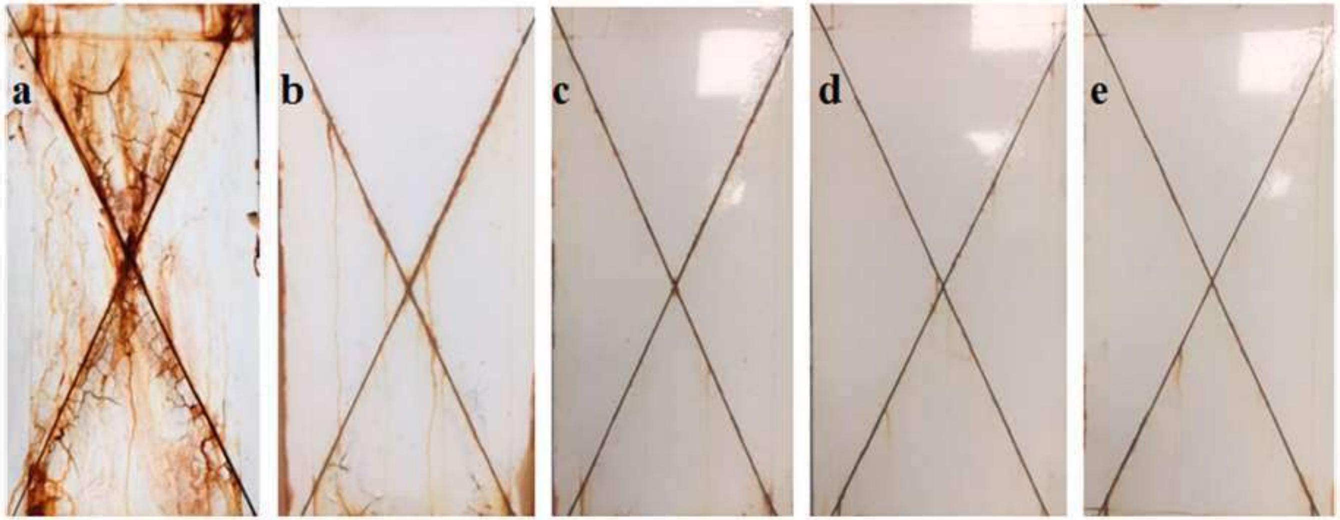
Test Methods	RP	CER1	CER2	CER3
Adherence/ASTM 3359	4B	3B	5B	5B
Hardness (Cycle)/DIN EN ISO 1522	24	39	45	45
Impact Resistance (weight, kg)/ASTM D2794	30	50	50	50

Color Differences	RP	CER1	CER2	CER3
ΔE	9.25 ± 0.2	3.40 ± 0.11	2.66 ± 0.12	2.93 ± 0.05
YI before UV	1.44	2.17	3.74	2.79
YI after UV	10.44	8.72	5.54	7.01





Color Difference	RP	CER1	CER2	CER3
ΔE	5.47 ± 0.08	3.88 ± 0.10	0.80 ± 0.19	2.51 ± 0.17



Test Parameter	Reference Test Method	Blank Coating	RP	CER1	CER2	CER3
Blistering (size)	ISO 4628-2	5	3	2	1	1
Blistering (density)	ISO 4628-2	5	3	2	1	1
Degree of rusting	ISO 4628-3	Ri5	Ri4	Ri4	Ri2	Ri3
Cracking (size)	ISO 4628-4	4	2	2	0	1
Cracking rate (quantity)	ISO 4628-4	4	3	2	1	1
Delamination (mm)	ISO 4628-8	21	13.5	9.5	6	6.5
Degree of delamination	ISO 4628-8	severe	moderate	slight	very slight	very slight

(**a**); reference material (RP) (**b**); 3 wt % cerium oxide microparticles (CER1) (**c**); 3 wt % cerium oxide nanoparticles (CER2) (**d**); 1 wt % cerium oxide nanoparticles (CER3) (**e**), after 672 h corrosion cycles under 5% NaCl solution

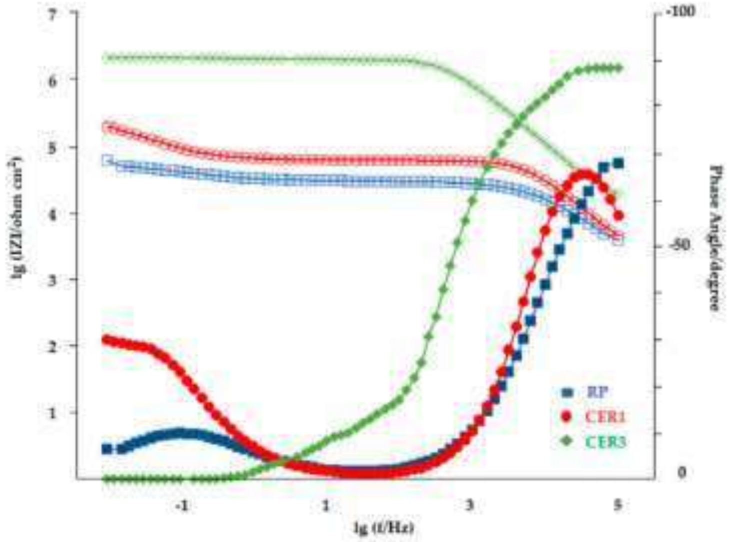


Figure 5. Bode plots of RP, CER1 and CER3 after immersion in 3.5% NaCl solution for 4 days (● Bode-phase plots, ○ Bode-magnitude plots).

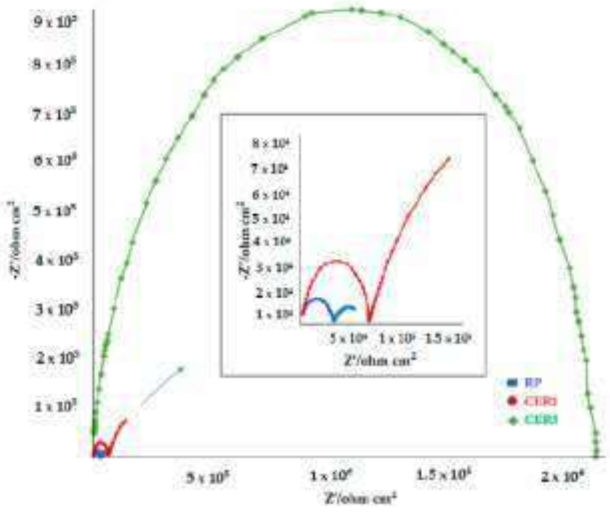


Figure 6. Nyquist diagrams of RP, CER1 and CER3 after immersion in 3.5% NaCl solution for 4 days.

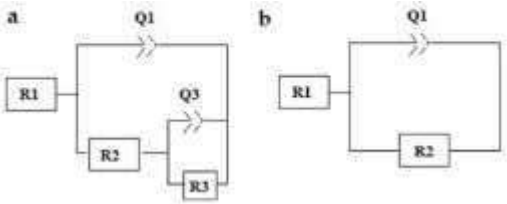


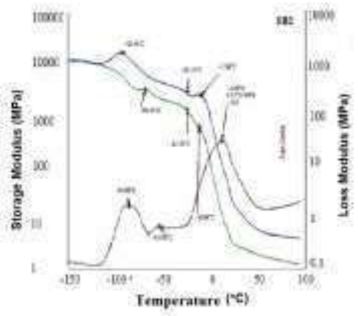
Figure 7. Equivalent electric circuits used to simulate the EIS results for the and CER3 (a) RP and CER1 (b).

Table 7. Data of EIS results from the equivalent circuits which were obtained from EC Lab Fitting Software for RP, CER1, and CER3 after immersion in 3.5% NaCl solution for 4 days.

Sample	Q1 (Q2), F cm^{-2}	n1	R2, Ω cm^2	Q3, F cm^{-2}	n2	R3, Ω cm^2	|Z| at 0.01 Hz (Ω cm^2, log10)
RP	6.34×10^{-9}	0.79	31,100	6.30×10^{-5}	0.62	28,102	4.8
CER1	7.6×10^{-10}	0.95	61,299	2.84×10^{-5}	0.71	295,380	5.3
CER3	3.77×10^{-10}	0.91	2,142,000	–	–	–	6.32

EXPERIMENTALS

Acrylic Paint Preparation → Physical Tests → Performance Tests → Antibacterial Activity (ISO 22196)



Paint Formulation & Physical Properties

Sample Name	SB0 wt. %	SB1 wt. %	SB2 wt. %
Styrene Acrylic Binder	45	45	45
Fillers	24	24	24
Additives*	7,05	7,05	7,05
Water	23,95	18,95	22,95
CeO_2 - 5 micron	-	5	
CeO_2 -25 nm	-		1
Total	100	100	100

*Calgon, HEC, Dispersion agent, Rheology agent, MPG, Texanol

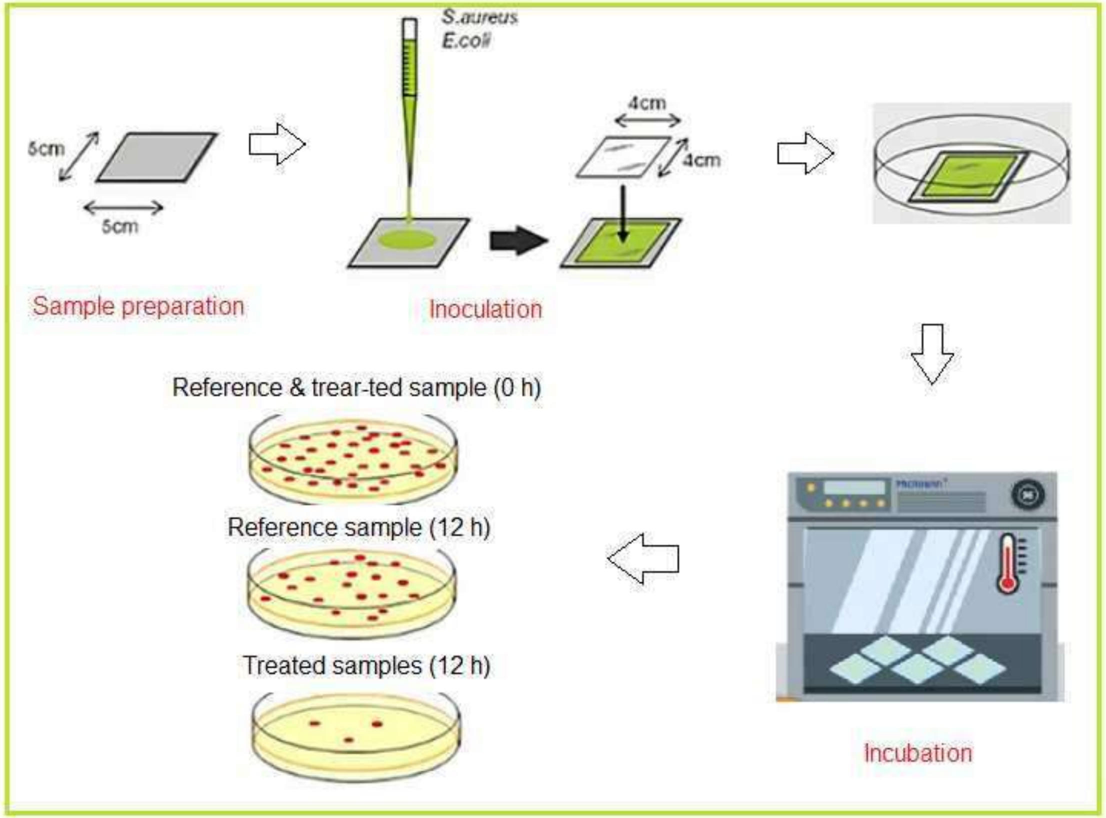
No any other pigments or biocides in formulations.

Physical Properties	Test Method	SB0	SB1	SB2
pH		8,07	8,25	8
Density (25°C), g/mL	ISO 2811-1	1,21	1,26	1,22
Viscosity (25°C), cps	ASTM D 2196	8060	9200	8800
Fineness of grind (micron)	ISO 1524	<10	<10	<10

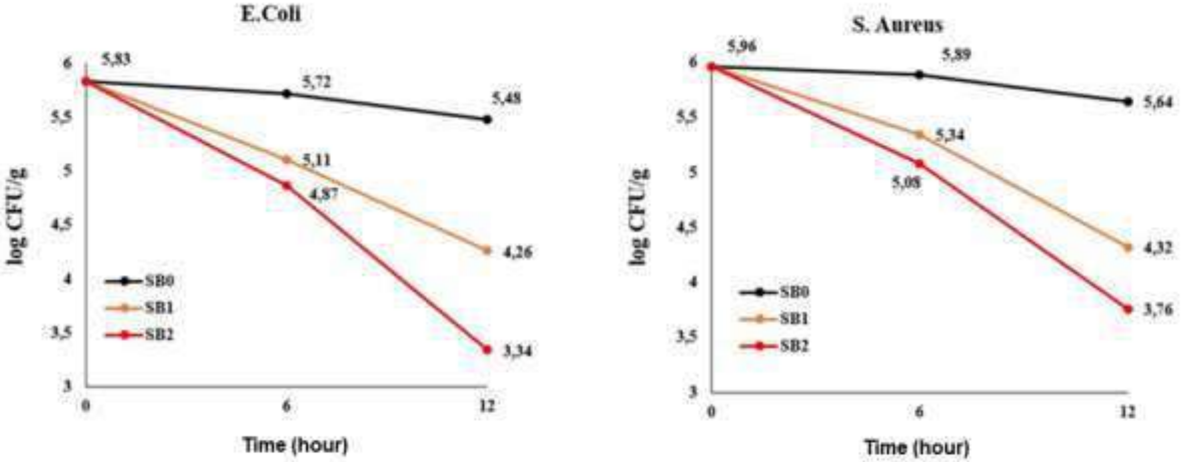
Performance Tests

	Test Method	SB0	SB1	SB2
Wet Scrub Resistance (µm, Ldft)	ISO 11998	4,3 ± 0,29	3,2 ± 0,14	2,9 ± 0,21
Classification of Wet Scrub Resistance		Class 1	Class 1	Class 1
Water Transmission Rate ($kg/m^2h^{0,5}$, W)	EN 1062-3	0,092 ± 0,0030	0,008 ± 0,0014	0,013 ± 0,0023
Classification of Water Transmission Rate		W3	W3	W3
Water Vapor Transmission Rate ($g/d*m^2$, V)	ISO 7783:2011	70,2 ± 3,40	140,3 ± 9,56	153,9 ± 13,13
Diffusion Equivalent Air Layer Thickness (m, sd)		0,29 ± 0,014	0,15 ± 0,010	0,13 ± 0,011
Classification of Water Vapor Transmission Rate		V2	V2	V1
Glass Transition Temperatures (^oC)	Dynamic Mechanic Analysis	13,10	11,96	14,80
Hardness (cycle)	DIN EN ISO 1522	20	29	35

Antibacterial Activity



Diagrammatic representation of Antibacterial Test Method - ISO 22196



Log Reduction Results of Antibacterial Tests

Log Reduction & %Reduction

E. Coli			
HOUR	CFU/sample		
	SB0	SB1	SB2
0	670000		
6	520000	130000	74000
12	300000	18000	2200
HOUR	Log CFU/sample		
	SB0	SB1	SB2
0	5,83		
6	5,72	5,11	4,87
12	5,48	4,26	3,34
HOUR	Log Reduction		
	SB0	SB1	SB2
6	0,1	0,7	1,0
12	0,3	1,6	2,5
HOUR	% Reduction		
	SB0	SB1	SB2
6	22,4	80,6	89,0
12	**55,2**	**97,3**	**99,7**

Staphylococcus Aureus			
HOUR	CFU/sample		
	SB0	SB1	SB2
0	920000		
6	770000	220000	120000
12	440000	21000	5700
HOUR	Log CFU/sample		
	SB0	SB1	SB2
0	5,96		
6	5,89	5,34	5,08
12	5,64	4,32	3,76
HOUR	Log Reduction		
	SB0	SB1	SB2
6	0,1	0,6	0,9
12	0,3	1,6	2,2
HOUR	% Reduction		
	SB0	SB1	SB2
6	16,3	76,1	87,0
12	**52,2**	**97,7**	**99,4**

*Microbiology tests have been carried out at Necmettin Erbakan University microbiology laboratories under the authority of Prof. Dr. Emrah Torlak.

Conclusion

Paints with Nanoceria

Alkyd Resin Solvent Based Metal Paints

- Self-Cleaning
- Resistance to UV-Aging
- Good Shelf Life
- Improved Adhesion, Hardness and Impact Resistance
- Anti-Corrosion

Acrylic Resin Water-Based Decorative Paints

- Anti-Bacterial
- Hardness
- Water Transmission Rate
- Water Vapor Transmission Rate
- Wet Scrub Resistance

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Special thanks to Prof. Dr. Fatma Bedia Erim Berker and Prof. Dr. Emrah Torlak.

Thanks to my colleagues at Polisan Kansai Paint and Istanbul Technical University...

and Thank you for your attention!