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A New Formulation Addressing Base Resin Challenges and Carcinogenic Concerns for Water Pipeline Cathodic Protection

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Abstract. Traditional epoxy coatings used for water pipeline cathodic protection suffer from several limitations, including restricted availability, high cost, and concerns regarding carcinogenicity. To overcome these challenges, we developed a new, affordable, food-grade epoxy coating that fulfils all technical requirements and lacks carcinogenic substances. The study involved experimenting with various reinforcing and non-reinforcing fillers, red pigment, and BYK additives to formulate the epoxy-based coating. Curing experiments followed, where the coating was formulated with a fixed curing agent ratio and sprayed onto mild steel panels for testing. The results revealed that the new formulation possesses good compressive strength, adequate impact resistance, and Shore D hardness within the expected range (60-70) for this application. Additionally, abrasion resistance was observed to increase with increasing hardness. In conclusion, the new food-grade epoxy coating presents a promising alternative to traditional options for water pipeline cathodic protection due to its affordability, adherence to technical requirements, and lack of carcinogenic substances.

Introduction

Coatings are used on buried pipelines to protect them from corrosion [1]. Cathodic protection is also used for this purpose, but it is considered the second line of defence in the gas/oil storage, transmission, and distribution sectors [2]. Therefore, today's coatings must provide better protection than their predecessors, be able to function under severe operating conditions, and be easy to apply even when conditions are less than ideal. Additionally, they must be a cost-effective solution for maintaining pipeline integrity.

The important parameters for corrosion protection are the adhesion of the coating to the pipeline surface and the resistance of the coating to the permeation of water, oxygen, and/or ions [3]. The major factors that affect the performance of protective coatings, according to NACE Standard RP0169-96 Section 5, are: a) surface preparation, b) wetting, c) bonding, and d) adhesion-cohesion phenomena [4].

Pipeline coatings are typically applied in three ways:

- Fusion bonded epoxy powder coating
- Application of multilayer coatings, such as three-layer polyethylene/propylene
- Thermoplastic polymer coating [5]

Epoxy coating is a preventative treatment that improves the quality of water in pipes and can serve as a frontline defence against corrosion, erosion, leaks, mold growth, and premature failure of metal pipes [6]. The rate of corrosion is inversely proportional to the resistivity of the electrolyte and directly proportional to the electron flux. Applying a high-resistive polymeric solution (such as epoxy, vinyl, or chlorinated rubber) and increasing its thickness on a still surface can improve resistance and, consequently, corrosion protection. Similarly, using inhibitive pigments in coatings, such as zinc chromate, red lead, and zinc phosphate, can further improve corrosion resistance of pipeline surfaces [7].

The spray-on-lining procedure for epoxy-resin coatings typically involves steps as drying the pipes, cleaning the pipes with pressure and sandblasting, applying the epoxy mass with pressure, and drying the coating. The pipes are ready to be flushed and used within 12-24 hours after the coating procedure is complete. This process is less expensive and non-invasive than traditional pipe replacement, which is why it became popular in Europe and the USA in the 1980s and 1990s [8-13]. However, there were several challenges associated with the spray-on-lining process, including:

- Proper cleaning of the inner surface of the pipe
- Finding a formula with a suitable curing time
- Efficiently spreading the lining materials

All these factors are essential for ensuring that the resin adheres properly to the pipe and does not leach into the oil or water. Epoxy coatings used in pipeline applications are typically two-part liquid epoxy systems, consisting of an epoxy resin component and a hardener component. Due to the presence of several toxic leaching ingredients, such as bisphenol A (BPA), diglyceryl ether (BADGE), and other organic compounds, epoxy-based coatings are not allowed in Germany and are not recommended in Sweden [14-16]. Additionally, epoxy coatings are subject to strict country-specific regulations and procedures. Recently, the price of food-grade epoxy resin has increased dramatically due to limited availability and rising base epoxy resin prices. This has caused the profit margin for food-grade epoxy coatings to decrease. Other manufacturers offer less expensive epoxy coatings, but these are not food-grade and contain Triethylenetetramine (TETA), which is a carcinogen [17-20]. In response to these challenges, in this paper, development of a fully food-grade epoxy resin is discussed that does not contain TETA or any related materials.

2. Experimental

2.1. Materials

Liquid epoxy base resin with an epoxy equivalent weight of 185-194 g/eq (grams per equivalent) and a viscosity of 11,000-14,000 cps at 25°C was sourced from Aditya Birla Chemicals. Diluents (reactive/non-reactive), cashew nutshell liquid, and reaction products with 1-chloro-2,3-epoxypropane were procured from Ark Golden India Pvt Ltd. The hardener used was an amine-based hardener, specifically a Mannich adduct of cardanol, formaldehyde, and amine from Ark Golden India Pvt Ltd. Namlon T 206, a thixotropic agent, was purchased from Unique Enterprises, Mumbai. Fumed silica (anti-sag agent and anti-settling agent) was obtained from Evonik, Germany.
The preparation of coating:

- Various kinds of reinforcing and non-reinforcing fillers were purchased from local sources.
- Red pigment, namely inorganic red pigment, was supplied by Cathay Industries Asia Pacific Limited, Hong Kong.
- BYK additives, namely BYK A530 (Defoamer and Releasing additive) and BYK 9076 (Deflocculates), were used for the formulation of the epoxy-based coating.
- The curing experiments of the prepared resins were formulated as liquid epoxy coatings with a fixed ratio of curing agent (3:1 volume of Resin: Hardener).
- The resin part was heated to 60-70°C before mixing for ease of application without sagging.

2.2. Testing of the coatings

These resins were sprayed (by using an air spray gun) with wet film thickness, WFT, 400 μ. It is common to use mild steel panels (15 cm×l0 cm) to evaluate the different properties of coatings. The other side of panels were coated against corrosion environments by using coal tar epoxy primer. The tested side was blasted and afterward cleaned to apply the coating materials. Then the panels were subjected to different testing procedures to assess the mechanical properties as well as durability.
Adhesion strength (Pull-off ASTM D4541), Dielectric strength (ASTM D 149), Electrical continuity inspection (NACE SP 0188),Cathodic disbondment test (ASTM G8), Immersion resistance test in a) Deionised water, 2) Conc. H_2SO_4 (1 % by Wt.), 3) Sodium hydroxide (1 % by Wt.) (AWWA C210), Cure test (ASTM D 5402), Tabor/ Abrasion resistance (ASTM D 4060) and Compressive strength (ASTM D 695) were measured. Sag tests were conducted at 5, 15, and 25 minutes upon mixing base

and hardener. All variants were cast on 150 mm X 150 mm tin plates, using a 200-1000 µm sag index applicator. The viscosity of the variants was measured by a Brookfield Viscometer (using mostly Spindle 04 at 60 rpm) at 25 °C.

3. Results and Discussion

The Viscosity and Sag test is done for all the samples in the similar conditions mentioned below. The viscosity value of tested samples having different compositions is provided in Table 1 as well as in Figure 1. To compare the viscosity of standard sample with a prepared sample at different temperature, the composition F3 was chosen, and they are comparative results are summarized in Table 2. The viscosity test was done at approx. 67 °C, 63 °C and near 60 °C temperature i.e., the application the temperature of the FGE material and the sag test was done with the mixture of 1:0.2 weight ratio of epoxy and hardener (ark 185) respectively.

Table 1. Viscosity and mixing ratio of different composition used for preparation of Epoxy coating formulation

Composition	Density - Comp A (Kg / Lit)	Viscosity @ 25 °C (Comp A)	Viscosity @ 60 °C (Comp A)	Mixing Ratio (By Wt.)	Mixing Ratio (By Vol)
F1	1.65	19640	1316	100: 20.20	3: 1
F2	1.60	27000	1764	100: 20.83	3: 1
F3	1.65	25880	2463	100: 20.20	3: 1
F4	1.61	26720	2149	100: 20.49	3: 1

Table 2. Effect of temperature on viscosity of standard and single composition

Viscosity	Temperature in Degree Celsius			
(cps)	67°	63°	60°	27°
Standard	2012	2100	2438	248800
F3	2076	2100	2463	257300

Table 2 provides the comparison of the viscosity test done at both the labs. As per the data given above, viscosity test results were quite similar in both the labs and within the application range at elevated temperatures of over 60 °C.

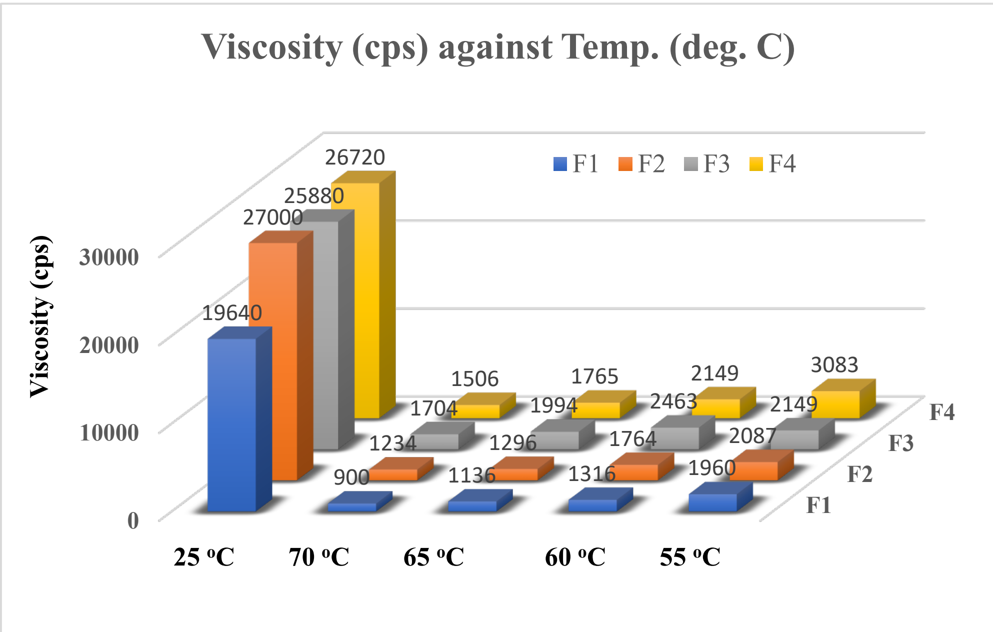


Fig. 1. Viscosity against temperature of different composition used for preparation of Epoxy coting system

For the testing of Sag properties, the epoxy was heated up to 60 ºC temperature and hardener was heated up to 40 ºC and then mixed thoroughly and then with the help of an 800-micron applicator the mixed epoxy was applied on a 40 ºC heated metal panel to observe the sag. The sag test carried out at different location had given promising results and as per the norms, it passed the test [15].

Mechanical Testing: In past two years, various coating systems (different formulations) have been tested to investigate their potential use as an internal pipeline coating. In this paper, we will deliberately introduce three coating systems that were subjected to mechanical tests. Results of the mechanical testing are presented in Table 3 which is given below.

Table 3. Mechanical Testing of Various Formulations for Internal Pipeline Coatings [a]

Coating System	**Pull off adhesion** (psi)	**Compressive strength** (MPa)	**Abrasion Resistance** (using CS 17 wheel, 1kg load for 1560 cycles)	**Hardness** (Shore D) After 7 days	**Impact Resistance** (after full cure), 2.1 Kg wt., Height 100 c.m.	**Cathodic Disbondment Test** (Maximum 10 mm (As per AWWA C210-15)
Test Standard	800 psi (as per AWWA C210-15 & Sauni Yojna)	Minim 70 MPa	>1560 cycles / mil (as per Sauni yojna)	80	Passed	Maximum 10 mm
A	Passes 1500 psi	71 Mpa	Passed (20500 cycles / mil)	62-64	Passed	9 mm
B	Passes 1550 psi	74 Mpa	Passed (20800 cycles / mil)	67-69	Passed	9 mm
C	Passes 1350 psi	69 Mpa	Passed (20500 cycles / mil)	67-68	Passed	10 mm

[a]All properties were measured a per the applicable test standard methods; therefore, reported values are average of multiple trails.

All three coatings (A, B, and C) showed pull-off adhesion strength in the 80-900 psi range, which is typical for good coating systems. All coatings failed primarily adhesively, indicating that the pull-off strength obtained is near the maximum value for the coating. All coatings showed good abrasion resistance, but coating C had the lowest compressive strength at 130 psi.

In various applications, cured epoxy is subjected to axial loads or forces. In these applications, an epoxy with a high compressive strength is the best choice to resist these forces continuously without being crushed. All the coatings in this study have good compressive strength.

The coatings showed slightly lower hardness (Shore D) values than the standard coating (all in the range of 60-70). This is expected for these types of coatings. However, a coating used for an internal pipeline should have adequate impact resistance to withstand accidental or unavoidable impact during placement and compaction. All the coatings in this study have adequate impact resistance.

Hardness is proportional to the abrasion resistance properties of a coating. As expected, the abrasion resistance of the coatings increased with increasing hardness. Hardness also indirectly proves the degree of cure of a coating, and it is important for comparative purposes or determining the degree of cure. The prepared coating showed comparatively less hardness and impact resistance properties in comparison to the standard coating system, but this does not have a significant impact on the coating's performance in its intended application.

Dielectric strength depends on the thickness of the specimen and the test temperature [16]. It provides an idea about the insulating strength of the materials. According to Sauni Yojna, the dielectric strength should be at least 250 V/mil. All the coatings in this study had dielectric strength values of at least 400 V/mil (Table 4).

Electrical continuity is defined as the ability to conduct electric current. This test was performed on all the coatings, and no holidays (film discontinuities) were observed (Table 4). This test method provides an idea of whether the protective system can be used for a specific application without showing any film discontinuities that are not readily visible to the naked eye.

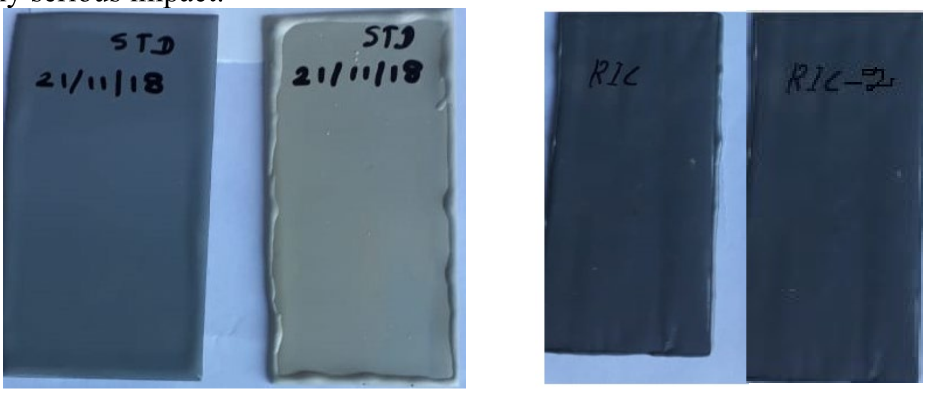
Table 4. Electrical Testing of Various Formulations Used for Internal Pipeline Coatings [a]

Sr. No.	Test Parameters	Test Method	Value Observed
1	**Dielectric Strength** (Min. 250 V/mil); a mil is 1/1000 inch	ASTM D149	≥ 400 V/mil
2	**Electrical Continuity Inspection**	NACE SP 0188	No Holiday observed

Chemical immersion studies were conducted according to the ASTM D 543 standard on formulations cured for 7 days at 25°C. One inch by three-inch (1" x 3") samples of 1/8" thick castings were prepared and fully immersed in reagents, specifically H2SO4, NaOH, and deionized water. Two samples of the standard formulation and one of the prepared solutions were immersed in each reagent, and the physical appearance of each immersion was observed after 28 days.

By simply comparing the 28-day immersion test results, all the prepared solutions did not change much except for a shade variation/colour change, as shown in Figure 2, Figure 3 and Figure 4, in terms of physical appearance compared to the standard solution used for pipeline coating.

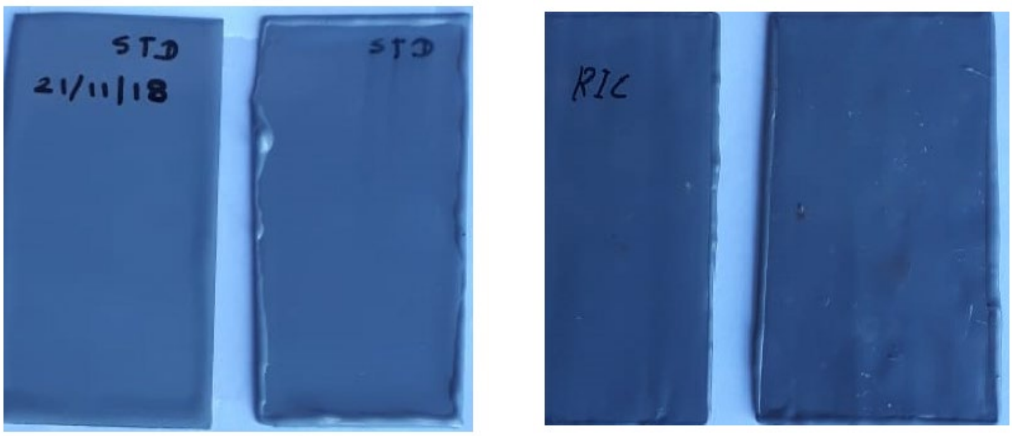
Similarly, cathodic disbonding studies were also conducted. Various parameters play a significant role in cathodic disbonding, such as electrolyte composition, the presence of hypochlorite in the electrolyte, dry film thickness, oxygen concentration in the electrolyte, and applied potential [17]. Samples for cathodic disbonding studies were given a circular holiday in the middle (6 mm in diameter) and polarization was done with a potentiostat. Table 5 shows that the new formulation did not have any serious impact.



Sample 1: LHS Panel: Unexposed, RHS Panel-Exposed

Sample 2: LHS Panel: Unexposed, RHS Panel-Exposed

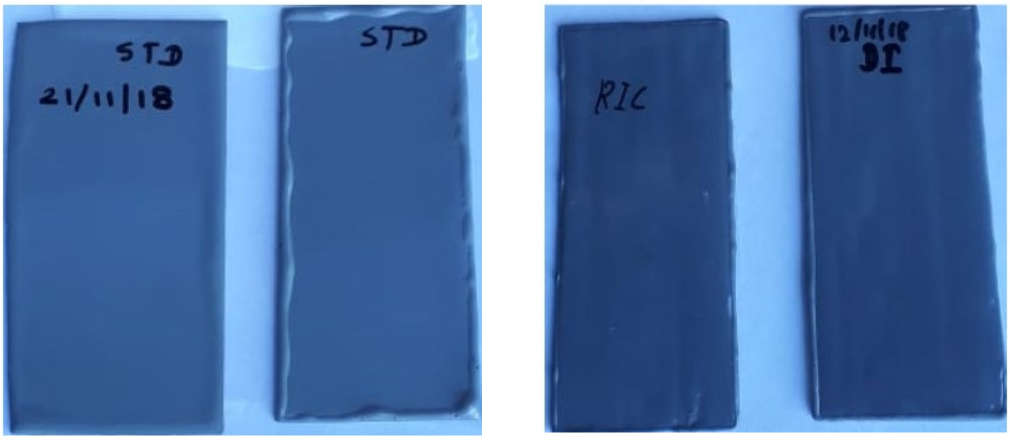
Fig. 2. Exposure in 1 % H_2SO_4 for 28 solution Days



Sample 3: LHS Panel: Unexposed, RHS Panel-Exposed

Sample 4: LHS Panel: Unexposed, RHS Panel-Exposed

Fig. 3. Exposure in 1 % KOH solution for 28 Days



Sample 5: LHS Panel: Unexposed, RHS Panel-Exposed

Sample 6: LHS Panel: Unexposed, RHS Panel-Exposed

Fig. 4. Exposure in DI water for 28 days

When the hardener is added, the resin will become more viscous and eventually lose its ability to flow, which is called the gel point of the resin system [16]. The gel time of both the standard and prepared resin formulations at room temperature and at a higher temperature of 40°C were measured. The gel time of the standard resin at room temperature was observed to be around 27 minutes, while all the new formulations had gel times in the range of 25-27 minutes. Similarly, at a higher temperature (e.g., 40°C), the gel time of the newly prepared solutions was slightly lower than that of the standard solution (e.g., 7 minutes for the standard solution and 6.2 minutes for recipe B).

Table 5. Gel time value for Sample A and Sample B

Sample No	Gel time value std. material	Get time value of new material
A	26 min @ RT	27 min @RT
B	7-8 min @ 40 ºC	6.2 min @ 40 ºC

Epoxy resin without solvent does not change its shelf life much if it is stored in a sealed container in the appropriate environmental conditions [19-20]. However, the resin may crystallize, or the hardener may darken, but this does not affect the performance of the epoxy resin. This is especially useful for warehouses where the materials are stored for prolonged periods of time.

Table 6. Shelf life of new formulation

S No	Item	Self-life
1	Standard formulation	2 years
2	New formulation	2 years

In this study, shelf life as measured is shown in Table 6. Samples were kept for 2 years and used it for coating. It was found that the gel time has increased with issues with surface adherence.

4. Conclusions

In conclusion, the new food-grade epoxy coating has good compressive strength (≥ 30 MPa), adequate impact resistance (≥ 10 J/m), and Shore D hardness in the range of 60-70. While the new formulation has slightly lower hardness and impact resistance than the standard coating system, this does not significantly impact its performance in its intended application. Overall, the new food-grade epoxy coating is a promising alternative to traditional epoxy coatings for water pipeline cathodic protection, with comparable technical properties and without the associated health concerns.

Disclosure of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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References

[1] F. O. Kolawole et al., "Mitigation of Corrosion Problems in API 5L Steel Pipeline – A Review," J. Mater. Environ. Sci., vol. 9, no. 8, pp. 2397-2410, 2018.

[2] L.T. Popoola, A.S. Grema, G.K. Latinwo, B. Gutti, A.S. Balogun, "Intern. J. Indus. Chem.," vol. 35, no. 4, pp. 1, 2013.

[3] J. Anthony von Fraunhofer, "Adhesion and Cohesion," Int. J. Dent., vol. 2012, Article ID 951324, 8 pages, 2012.

[4] Johanna Rajasarkk et al., "Drinking Water Contaminants from Epoxy Resin-Coated Pipes: A Field Study," vol. 103, pp. 133-140, 2016.

[5] A. Jones, B. Smith, "Advancements in Epoxy Coatings for Corrosion Protection: A Comprehensive Review," J. Mater. Sci. Technol., vol. 25, no. 3, pp. 315-330, 2009.

[6] R. Kumar, S. Gupta, "Recent Trends in Epoxy Resin Formulations and Applications," Prog. Polym. Sci., vol. 37, no. 3, pp. 340-368, 2012.

[7] M. Rahman, S. Khan, "Food-Grade Epoxy Coatings: Challenges and Developments," J. Coat. Technol. Res., vol. 14, no. 5, pp. 1075-1091, 2017.

[8] J. Li, C. Wang, "Carcinogenic Substances in Epoxy Resins and Alternatives for Food-Grade Applications," Mater. Today, Chem., vol. 13, pp. 17-26, 2019.

[9] N. Patel, P. Sharma, "Innovative Approaches in Epoxy Coating Technology for Corrosion Mitigation," Surf. Coat. Technol., vol. 280, pp. 125-134, 2015. DOI: 10.1016/j.surfcoat.2015.08.019

[10] Mohammad Khani et al., "Designing a dual-functional epoxy composite system with self-healing/barrier anti-corrosion performance using graphene oxide nano-scale platforms decorated with zinc-doped conductive polypyrrole nanoparticles with great environmental stability and non-toxicity," Chemical Engineering Journal, vol. 382, 2020, 122819. DOI: 10.1016/j.cej.2019.122819

[11] Trinh Anh Truc, et al., "8-hydroxyquinoline-modified clay incorporated in an epoxy coating for the corrosion protection of carbon steel," Surfaces and Interfaces, vol. 14, pp. 26-33, 2019. DOI: 10.1016/j.surfin.2018.10.007

[12] Feng-Qi Liao, Yung-Chung Chen, "Siloxane-based epoxy coatings through cationic photopolymerization for corrosion protection," Progress in Organic Coatings, vol. 174, 107235, 2023. DOI: 10.1016/j.porgcoat.2022.107235

[13] S. Mohammadkhah, et al., "Improvement of active/passive anti-corrosion/weathering properties of epoxy-siloxane structure via cloisite 30B/polyaniline inclusion as a new hybrid nanocomposite coating," Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 666, 2023. DOI: 10.1016/j.colsurfa.2023.131297

[14] Min Sun, Zhidong Ma, Anhang Li, Guiyu Zhu, Yue Zhang, "Anticorrosive performance of polyaniline/waterborne epoxy/poly(methylhydrosiloxane) composite coatings," Progress in Organic Coatings, vol. 139, 105462, 2020. DOI: 10.1016/j.porgcoat.2019.105462

[15] Y. Guo et al., "Preparation and performance of a composite epoxy coating based on modified hydroxyapatite," Surf. Coat. Technol., vol. 443, 128614, 2022. DOI:10.1016/j.surfcoat.2022.128614

[16] Y. Morozov et al., "Epoxy coatings modified with a new cerium phosphate inhibitor for smart corrosion protection of steel," Corros. Sci., vol. 159, 108128, 2019. DOI: 10.1016/j.corsci.2019.108128

[17] A.M. Atta et al., "Self-healing of chemically bonded hybrid silica/epoxy for steel coating," Prog. Org. Coat., vol. 141, 105549, 2020. DOI: 10.1016/j.porgcoat.2020.105549

[18] F. Presuel-Moreno, M.A. Jakab, N. Tailleart, M. Goldman, J.R. Scully, "Corrosion-resistant metallic coatings," Materials Today, vol. 11, no. 10, pp. 14-23, 2008. DOI: 10.1016/S1369-7021(08)70203-7

[19] Wufang Yang, Weibin Feng, et al., "Protection of mild steel with molecular engineered epoxy nanocomposite coatings containing corrosion inhibitor functionalized nanoparticles," Surface and Coatings Technology, vol. 406, 126639, 2021. DOI: 10.1016/j.surfcoat.2020.126639

[20] Zhenhua Zhang et al., "Self-healing nanocomposite coatings containing organic-inorganic inhibitors functionalized dendritic silica nanocontainers for synergistic corrosion protection of carbon steel," Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 656, Part A, 130430, 2023. ISSN 0927-7757. DOI: 10.1016/j.colsurfa.2022.130430