



The effect of TiO₂ Nanoparticles in Epoxy Paint Formulation on Metal Surfaces

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Currently, epoxy paint is being widely used in the industry. Nanotechnology can create many small nanometer-sized materials with many applications, it has brought many outstanding properties to epoxy paints. The aim of this study is to investigate the effect of TiO₂ nanoparticles in epoxy paint formulation towards metal surface. We created a sample of two-component epoxy paint, part A is epoxy resin, anti-sedimentation, dispersant substance, foam breaking agent, cover substance, solvent, other additives, and part B is a curing agent for epoxy resins. Methods of analyzing the properties of the epoxy paint film are based on Vietnam standards. TiO₂ nanoparticles are a good coating substance in epoxy paint. The study results showed that TiO₂ nanoparticles have increased the properties of the epoxy paint film, improving the Impact and Glossy of the epoxy paint film. TiO₂ nanoparticles increases from 1% to 6% by weight, the impact increased by about 18.75%. (80 to 96 kg.cm), Glossy 60° increased by about 12.79% (80 to 97). Adding TiO₂ nanoparticles to epoxy paint has increased Impact and Glossy for the paint film. The higher the rate of TiO₂ nanoparticles, the better the properties of the epoxy paint film. Therefore, TiO₂ nanoparticles are a good coating in epoxy paint, it improves the properties of the paint film. Because the cost of nanomaterials is higher than that of normal coating materials, the nanomaterial should only be added with a ratio of about 2-5% by weight.

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1. INTRODUCTION

Currently, epoxy paint is being widely used in the industry. Using epoxy paint to protect and reinforce metal and concrete surfaces increases the life of the building with many advantages such as beautiful glossy surfaces, diverse colors, anti-slip, waterproof, anti-abrasion [1,2]. Epoxy paint is paint with 2 components, part A is the paint part and part B is the curing agent. These two components mixed together in a certain ratio will produce a film with very high adhesion, the paint film has strong toughness, high gloss, abrasion resistance, solvent resistance, good chemical resistance, anti-static. electric, anti-rust, acid-resistant [3,4,5].

Part A is epoxy resin, anti-sedimentation, dispersant substance, foam breaking agent, cover substance, solvent and other additives. Epoxy resin is the most important ingredient for epoxy paint, it greatly affects the adhesion of the paint film. The properties of epoxy resins depend on the degree of reactivity and the molecular mass distribution of the polymer. The functional group of epoxy resin determines the thermomechanical properties of the resin. It can be classified into several different classes on the basis of the structure of the phenol-containing molecule and the number of phenol groups in each molecule [6,7,8].

Component B is a curing agent for epoxy resins, which helps bind epoxy molecules together. Currently, there are many methods of curing epoxy resin by chemical [9,10,11], and UV light [12]. Chemical curing agents such as polyamide, aromatic diamine with hetero-cyclic side chain structure, amido amide, cyclo aliphatic [13]. Polyamide is a medium viscosity epoxy curing agent, produced based on the dimerization of fatty acids and polyamines. This product has good chemical and corrosion resistance, good adhesion, and is waterproof [14].

Nano is a new field that is being studied and applied by scientists. Nanoparticles have a small particle size of less than 100 nm but a larger surface area than conventional particles. Studies show that nanomaterials have a small size with many outstanding properties, so they are widely used in medicine, electronics, optics, industry and life. Scientists are currently debating the implications of nanotechnology in the future. Nanotechnology poses many of the same problems as any new technology, including

concerns about the toxicity and environmental impact of nanomaterials [15].

Nanotechnology can create many small nanometer-sized materials with many applications, it has brought many outstanding properties to epoxy paints in terms of gloss, impact resistance, and reduced chemical and environmental corrosion [16,17,18]. Many kinds of nanomaterials such as nano TiO₂, nano CaCO₃, nano ZnO, nano BaSO₄, nano SiO₂, nano Fe₂O₃ have been studied and applied in epoxy paint [19]. The production of TiO₂ nanoparticles has also been noted to create nanoscale materials by various methods. Many studies on the properties of TiO₂ nanomaterials, the properties of paints with TiO₂ nanomaterials as coatings have been evaluated. There are still many problems in using nanomaterials as coatings in paints that need further research such as durability of paint films over time when replacing TiO₂ coatings with TiO₂ nanomaterials, the relationship between replacement rate and economic efficiency in using this paint [20,21,22]. TiO₂ nanoparticles have been studied and applied in many different aspects in epoxy coatings.

The purpose of this study is to investigate the effect of TiO₂ nanoparticles in epoxy paint formulation on metal surfaces.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Component A of epoxy

- Epoxy is the original epoxy resin of diglycidyl ether Bisphenol-A, it has excellent adhesion, chemical resistance, heat resistance. Epoxy YD 011X75 has been dissolved in xylene for easy use in applications, solid content is 75%. Made in Korea.
- Bentone 34 is a special clay mineral, it is a sodium-aluminum hydrosilicate. Bentone 34 is used to refer to natural stone, it is a very fine particle material that mainly consists of clay minerals. Made in China
- Cloparaffin is a clear or pale yellow liquid. Chlorine content: 51.7, Density (g/ml) at 25°C:1.26. Made in India
- Disper is an effective dispersant that disperses organic and inorganic additives in the paint to create a gloss for paint film. Chinese origin.

- Foamex N is effective against micro-foam in the stirring process. Germany origin.
- Airex 900 is a foam breaking agent, it breaks down bubbles formed in the process of grinding, mixing, to make the paint film glossy and smooth. Chinese origin.
- TiO₂ is a compound with a high melting point (heat resistance), little chemical effect (chemical resistance), abrasion resistance, large hardness but still remains stable, good plasticity, less cracking, TiO₂ has a high coverage, fine particles, good oil permeability and very durable under the effect of moist air, seawater. TiO₂ is not denatured over time, it is widely used in the paint industry. Made in China.
- TiO₂ nanoparticles is Particle size 5-30nm, purity 99.99%, white color, inertness, fine powder, dispersed in water and oil. This type of TiO₂ nanoparticles is often used as a coating for printing ink and paint with the rate used in the formula from 2-25%. TiO₂ nanoparticles have very good sun protection. The sun protection mechanism of TiO₂ nanoparticles is reflective of sunlight, protecting the painted object under radiation, so it has the ability to stabilize the coating to extend the life. Made in China.
- Barium sulfate is an inorganic compound with the chemical formula BaSO₄, Density: 4.49 g/cm³. It is an odorless white crystalline substance and is insoluble in water. Barium sulfate is used as a pigment as a coloring additive for the paint industry, which can increase adhesion, keep the color bright, and not fade. Made in China
- Methyl Isobutyl Ketone (MIBK) is a colorless liquid, with a ketone odor, density: 0.802g/cm³, freezing point: -84.7°C, boiling point: 117-118°C. Made in Korea.
- Cyclohexanone is a medium-volatile solvent, a transparent, high-boiling liquid with a characteristic ketone odor, with good solubility in many organic substances, insoluble in water. Made in the Netherlands
- Acetate butyl is a colorless liquid with a fruity aroma similar to that of a ripe banana, melting point: -74°C, boiling point: 126°C. Acetate butyl is the most commonly used solvent in the paint industry, helping to dry paint quickly while ensuring an even coating and good gloss. Made in Vietnam
- BYK 066 is defoamer for coatings, and ambient curing plastic systems on the basis of epoxy resin. Made in Germany.
- Xylene is a clear colorless liquid with a pleasant aroma. Auto-ignition temperature

500°C. Density at 20°C is 0.865-0.875 kg/l. This mixture is liquid, colorless. Made in China.

2.1.2 Component B of epoxy

Epicure 3125 is a polyamide type epoxy curing agent with medium viscosity, good chemical and corrosion resistance, good adhesion. Made in India.

2.2 Method of Creating Epoxy Paint Film

We created different paint formulations with the replacement rate of TiO₂ coating material by TiO₂ nanoparticles, then examined how the nanomaterials affect the properties of epoxy coating films. Each sample epoxy paint formulation is painted on 12 metal sheets measuring 70x150 mm and 0.5 mm thick with the same film thickness. It's quite difficult to create a coat of uniform thickness, so we have created many designs for you to choose from. A common tool for creating coatings in the lab is the manual film gauge. We used the manual scissors model BGD 201/5 with the 100 μm scale of the manufacturer Biuged. It is made of stainless steel with 2% accuracy, easy to use, produces a relatively uniform paint film. The paint film is created based on the Doctor Blade technique.

2.3 Method of Creating Epoxy Paint Samples

There have been some previous studies using nanomaterials in the paint at rates as low as 2-5% by weight. Thien and his colleagues investigated and supplemented in the nanocomposite coating containing 2 wt % nano-SiO₂ [23]. Priyanka A and his colleagues found that adding 5% by weight of nano-silica to polyurethane paint gave a good effect [24]. In this study, we investigated the addition of TiO₂ nanoparticles from 1-6% by weight to the formulations of epoxy paints.

We have created epoxy coating formulations C1, C2, C3, C4, C5, C6 and C7 with the same composition, only different in TiO₂ and TiO₂ nanoparticles. The percentage of TiO₂ nanoparticles in the above formulas increased from 1-6% by weight (Table 1).

2.4 Methods of Analysis

- Drying time of the paint film is determined according to Vietnam Standard TCVN [25].
- Coverage of dry paint film is determined according to TCVN [26].

- Gloss 60⁰ is determined according to TCVN [27]
- The impact is determined according to TCVN [28].

Table 1. Composition of epoxy paint formulations

N ^o	Component	Raw materials	Uses	C 1 Wt. %	C 2 Wt. %	C 3 Wt. %	C 4 Wt. %	C 5 Wt. %	C 6 Wt. %	C 7 Wt. %
1	Component A	Epoxy YD 011X75	Resin adhesion for paint	41	41	41	41	41	41	41
2		Bentone 34	Anti-sedimentation	0.3	0.3	0.3	0.3	0.3	0.3	0.3
3		Cloparafin	Plasticizer Additives, Chemical resistance	4	4	4	4	4	4	4
4		Disper 710S	Dispersant substance	0.4	0.4	0.4	0.4	0.4	0.4	0.4
5		Foamex N	Anti-foam	0.2	0.2	0.2	0.2	0.2	0.2	0.2
6		Airex 900	Foam breaking agent	0.4	0.4	0.4	0.4	0.4	0.4	0.4
7		TiO ₂	Cover substance	20	19	18	17	16	15	14
8		TiO ₂ nanoparticles	Cover substance	0	1	2	3	4	5	6
9		BaSO ₄	Cover substance	3	3	3	3	3	3	3
10		Xylen	Solvent	14	14	14	14	14	14	14
11		MIBK	Solvent	3	3	3	3	3	3	3
12		Cyclohexanone	Solvent	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13		Acetate Butyl	Solvent	2.0	2.0	2.0	2.0	2.0	2.0	2.0
14		BYK 066	Defoaming Additives	0.2	0.2	0.2	0.2	0.2	0.2	0.2
15	Component B	Epicure 3125	Solidifying agent	9	9	9	9	9	9	9
Total				100	100	100	100	100	100	100

3. RESULT AND DISCUSSION

Table 2. Properties of epoxy paint

No	Properties	Unit	C 1	C 2	C 3	C 4	C 5	C 6	C 7
1	Face dry time	minutes	27	27	27	27	27	27	27
2	Natural drying time	hours	10	10	10	10	10	10	10
3	Density 30 ⁰ C		1.21	1.21	1.21	1.21	1.21	1.21	1.21
4	Smoothly	µm	26	26	25	25	24	24	24
5	Impact level	kg.cm	80	82	86	90	93	95	96
6	Coverage of dry paint film	g / m ²	113	113	113	113	113	113	113
7	Glossy 60 ⁰		86	87	90	93	95	96	97

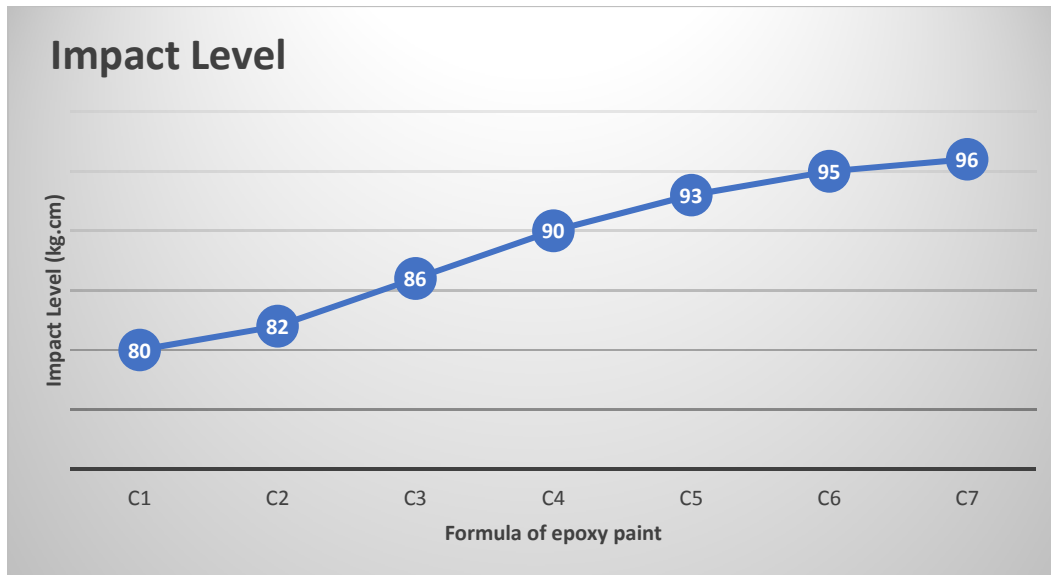


Fig. 1. Impact of epoxy paint formulations

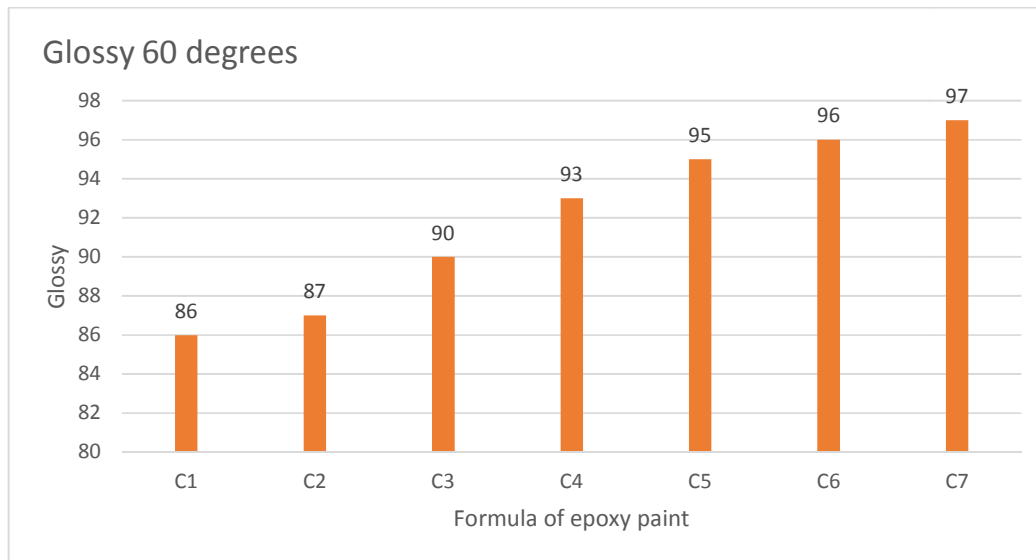


Fig. 2. Glossy 60° of epoxy paint formulations

The data and graphs in Fig. 1 and Table 2 show that with increasing concentration of TiO₂ nanoparticles, the degree of impact also increases. Impact of epoxy paint formulations 1 to 7 rapidly increased from 80 - 96 kg. cm when increasing the proportion of TiO₂ nanoparticles from 1 to 6% by weight. Without adding TiO₂ nanoparticles, Impact of C1 was 80 kg.cm, adding 1% of TiO₂ nanoparticles, Impact of C2 increased by 2.5%, adding 2% of TiO₂ nanoparticles, Impact of C3 increased by 7.5%, adding 3% of TiO₂ nanoparticles. TiO₂ nanoparticles, Impact of C4 increased by 12.5%,

adding 4% of TiO₂ nanoparticles, Impact of C5 increased by 16.25%, adding 5% of TiO₂ nanoparticles, Impact of C6 increased by 17.5%, adding 6% of TiO₂ nanoparticles, Impact of TiO₂ nanoparticles C7 increased by 18.75%. Thus, the Impact index increased rapidly when TiO₂ nanoparticles were added from 2 to 4% by weight.

The data and graphs in Fig. 2 and Table 2 show that as the concentration of TiO₂ nanoparticles increases, glossy also increases. Glossy 60° of epoxy paint formulations 1 to formula 7 increased

from 86 to 97. When not adding TiO₂ nanoparticles, Glossy 60° of C1 was 86, adding 1% of TiO₂ nanoparticles, Glossy 60° of C2 increased by 1.16%, adding 2% of TiO₂ nanoparticles, Glossy 60° of C3 increased by 4.65%, adding 3% of TiO₂ nanoparticles, Glossy 60° of C4 increased by 8.14%, adding 4% of TiO₂ nanoparticles, Glossy 60° of C5 increased by 10.46%, adding 5% of TiO₂ nanoparticles, Glossy 60° of C6 increased by 11.62%, adding 6% of TiO₂ nanoparticles, Glossy 60° of C7 increased by 12.79%. Thus, the Glossy 60° index increased rapidly when TiO₂ nanoparticles were added from 2 to 4% by weight.

The data and graphs in Fig. 2 and Table 2 show that when increasing the concentration of TiO₂ nanoparticles, the impact level and glossy 60° of the epoxy coating film also increase. This can explain that TiO₂ nanoparticles are very small and fine, so they create glossy on the metal surface. This issue has also been raised in some previous studies on nano coatings in paints. TiO₂ nanoparticles are oxide nanostructured particles with spherical or multifaceted high surface areas.

Incorporation of nanoparticles into epoxy resin is a solution to enhance coating durability as fine particles dispersed in the coating can fill the voids, reducing the porosity of the paint film. Nanoparticles can also prevent epoxy separation during curing, making the coating more uniform. Nanoparticles tend to reduce pore defects as a result of local shrinkage during epoxy resin curing. In addition, epoxy coatings containing nanoparticles will protect against corrosion and reduce the tendency of the coating to blister or delamination. In recent research, epoxy nanocomposites improve the mechanical, thermal and morphological anti-corrosion properties of the coating.

4. CONCLUSION

Adding TiO₂ nanoparticles to epoxy paint has increased Impact and Glossy for the paint film, it helps the paint film to resist the harmful effects of the environment. TiO₂ nanoparticles are a good coating in epoxy paint, it improves the properties of the paint film. Because the cost of nanomaterials is higher than that of normal coating materials, the nanomaterial should only be added with a ratio of about 2-5% by weight.

The study of adding nanomaterials to coatings has an important meaning, it not only gains many benefits in improving the properties of paint films but also contributes to proving and clarifying the

value of nanotechnology and its effective applications now and in the future.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Pan G, Wu L, Zhang Z, and Li D. "Synthesis and characterization of epoxy-acrylate composite latex. *Journal of Applied Polymer Science*. 2002;83:1736-1743.
2. Galliano and Landolt D. Evaluation of corrosion protection properties of additives for waterborne epoxy coatings on steel. *Progress in Organic Coatings*. 2002;44:217-225.
3. Sukanya P, Priyanka P, Smita M, and Sanjay KN. Insight on the Chemistry of Epoxy and Its Curing for Coating Applications: A Detailed Investigation and Future Perspectives. *Polymer- plastics technology and engineering*. 2016;55(8):862-877.
4. Ren H, Chen W, and Fan L. Study on the cure kinetics of a silicone-modified waterborne epoxy curing agent by the advanced isoconversional method. *Polymer-Plastics Technology and Engineering*. 2010;49:836-840.
5. Ramesh D and Vasudevan T. Synthesis and physico-chemical evaluation of water-soluble epoxy ester primer coating. *Progress in Organic Coatings*. 2009;66: 93-98.
6. Jin FL, Li X, and Park SJ. Synthesis and application of epoxy resins: A review. *Journal of Industrial and Engineering Chemistry*. 2015;29:1-11.
7. Murias, H. Maciejewski, and H. Galina. Epoxy resins modified with reactive low

- molecular weight siloxanes. *European Polymer Journal*. 2012;48:769-773.
8. Yang X, Huang W, and Yu Y. Synthesis, characterization, and properties of silicone-epoxy resins. *Journal of Applied Polymer Science*. 2011;120:1216-1224.
 9. Sun H, Ni W, Yuan B, Wang T, Li P, Liu Y, et al. Synthesis and characterization of emulsion-type curing agent of water-borne epoxy resin. *Journal of Applied Polymer Science*. 2013;130:2652-2659.
 10. Zhou JI and Tu WP. Synthesis of nonionic type self-emulsified waterborne epoxy curing agent and its properties. *Journal of Chemical Engineering of Chinese Universities*. 2006;20:94.
 11. Guangqi L, Jianzhong S, and Qiyun Z. Synthesis and characterization of waterborne epoxy curing agent modified by silane. *Chinese Journal of Chemical Engineering*. 2007;15:899-905.
 12. Wang X, Wang X, Song L, Xing W, Tang G, Hu W, et al. Preparation and thermal stability of UV-cured epoxy-based coatings modified with octamercaptopropyl POSS. *Thermochimica Acta*. 2013;568:130-139.
 13. Ghaemy M, Barghamadi M, and Behmadi H. Cure kinetics of epoxy resin and aromatic diamines. *Journal of Applied Polymer Science*. 2004;94:1049-1056.
 14. Xiong X, Ren R, Liu S, Lu S, and Chen P. The curing kinetics and thermal properties of epoxy resins cured by aromatic diamine with hetero-cyclic side chain structure. *Thermochimica Acta*. 2014;595:22-27.
 15. Barbara MR, Samuel S, Beat H, Nadine K, and Peter G. Interaction of Fine Particles and Nanoparticles with Red Blood Cells Visualized with Advanced Microscopic Techniques. *Environmental Science & Technology* 2006;40(14):4353-4359.
 16. Tuan AN, Huyen N, Thien V N, Hoang T. Effect of Nanoparticles on the Thermal and Mechanical Properties of Epoxy Coatings. *Journal of Nanoscience and Nanotechnology*. 2016;16(9):9874-9881.
 17. Zahed A. Epoxy in nanotechnology: A short review. *Progress in Organic Coatings*. 2019;132:445-448.
 18. Xianming S, Tuan AN, Zhiyong S, Yajun L, Recep A. Effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coating. *Surface and Coatings Technology*. 2009;204:237-245.
 19. Tamayo-Aguilar A, Guaman MV, Guerrero VH, Lagos KJ, Costa CA, Nascimento CR, Marinkovic BA, Ponton PI. Mechanical properties of amine-cured epoxy composites reinforced with pristine protonated titanate nanotubes. *Journal of Materials Research and Technology*. 2020;9(6):15771-15778.
 20. Li BR, Wang XH, Yan M Y, Li LT. Preparation and characterization of nano-TiO₂ powder. *Material Chemistry Physics*. 2003;78(1):184-188.
 21. Zhang J, Shi L, Zhu W, Wang X. Preparation and properties of nano-TiO₂ modified interior wall paint. *Journal Shanghai University (English Edition)*. 2007;11(4):432-436.
 22. Hsu L and Chein H. Evaluation of nanoparticle emission for TiO₂ nanopowder coating materials. *Journal of Nanoparticle Research*. 2007;9:157-163.
 23. Thien VN, Tuan AN and Hau NT. The Synergistic Effects of SiO₂ Nanoparticles and Organic Photostabilizers for Enhanced Weathering Resistance of Acrylic Polyurethane Coating. *Journal of Composites Science*. 2020;4(1):23.
 24. Priyanka A, Swati G, Ravindra GP. Development and Evaluation of Nano-Silica Dispersed Polyurethane Based Coatings for Improved Anti-Graffiti and Scratch Resistance. *Open Journal of Applied Sciences*. 2015;05(12):808-818.
 25. TCVN: Method of determining dry time. 2015;1:2096.
 26. TCVN 2095-1993: Method of determining the coating coverage.
 27. TCVN 9014:2011: Method of determining the gloss of epoxy paint.
 28. TCVN 2100-2-2007: Method of determining the impact of paint.

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