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Partial replacement of $CaCO_3$ with Nano $CaCO_3$ to protect metal surfaces

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Abstract

Objectives: Nanomaterials are currently being studied and used in paints. The purpose of this study is to investigate the properties of alkyd paint to protect metal when replacing $CaCO_3$ by nanomaterial. **Methods/ analysis :** Using the method of replacing $CaCO_3$ coating by $CaCO_3$ nanomaterials with different proportions in traditional paint formulas, the experiment is performed on tin plate and measuring, analyzing, evaluating the durability indexes according to time. Methods of analyzing properties of paint films based on Vietnamese standards used to measure the properties of paint films. **Findings**: Replacing $CaCO_3$ coating material with $CaCO_3$ nanomaterial has increased the superiority of alkyd paint to protect metals. The higher the replacement rate, the higher the measure of the properties of the paint film, the impact increased by about 13% (70 to 79 kg.cm), Glossy 60^0 increased by about 10%, Glossy 85^0 increased by about 9%. Especially, the durability of paint film over time is nearly double when completely replace the $CaCO_3$ coating with $CaCO_3$ nanomaterials. However, $CaCO_3$ nanomaterials are much more expensive than $CaCO_3$ so in practice they should only replace less than 8% by weight. For projects requiring high quality, a higher rate may be used. **Novelty/Applications**: The novelty of the study is the replacing $CaCO_3$ with Nano $CaCO_3$; this replacement confirms the effectiveness of nanomaterials and helps paint manufacturers choose the replacement rate suitably.

Keywords: Adhesion; coatings; durability; glossiness; impact level; long life

1 Introduction

Nano $CaCO_3$ is a nanometer-sized material that is interested in research and application because it is a common material, has many advantages and the synthesis path to create it is not too difficult. It is used in the sterilization of libraries[(1)], hospitals, textiles and as coating materials in paints. Scientists prepared $CaCO_3$ nanoparticles with various methods such as fine grinding from large size particles into small size particles or chemical precipitation for small size. The synthesis of calcium carbonate nanoparticles by precipitation using high pressure also has a lot of advantages. Calcium carbonate nanoparticles were synthesized by reactive precipitation of sodium carbonate and calcium chloride solutions using a high- pressure jet homogenizer in the presence of sodium caseinate as a stabilizer to produce nanoparticles (z-average = 100 nm)[2]. Moreover, the synthesis of nanoparticles calcium carbonate by reactive precipitation using high pressure nowadays is very popular. This method has many benefits to create nano $CaCO_3$ which are suitable for the paint industry. $CaCO_3$ nanoparticles with about 50 nm in size could be prepared by the carbonation reaction of a mixture of $Ca(OH)_2$ and dodecyl dimethyl betaine via bubbling CO_2 gas[3].

In the field of paints, there are many types of nanomaterials that have been researched with lots of applications such as nano TiO_2, Al_2O_3, SiO_2, ZnO, $CaCO_3$[4]. Nano $CaCO_3$ with a size of about 50-100nm is a nanomaterial that has been studied and applied in the paint industry because it has many characteristics such as preventing the effect of ultraviolet rays, creating gloss for metal surfaces and being a protective metal coating preventing environmental impacts. There have been some studies for surface modification of Nano $CaCO_3$ at room temperature to improve the surface of paint films[5]. $CaCO_3$ nanomaterials are applied in polyurethane paint (PU), epoxy paints, and some other coatings that have increased the durability and gloss of paints[6,7]. The emulsion paint prepared with nanoparticles of precipitated calcium carbonate (NPCC) showed better wet-state storage stability of the coating, greater abrasion resistance, lower roughness, and lower wettability than the conventional paint[8]. The research team of Juan D. Olarte-Plata researched the impact of nanoparticle roughness on the phase behavior of suspensions in models of calcium carbonate nanoparticles[9].

The field of research using nano $CaCO_3$ as a coating is a new field, which is not fully studied about the properties of paint films. Many studies investigate the properties of paint films such as surface dryness, glossiness, impact but less research on the life of paint films when coating metal, therefore, this field needs further study to fully evaluate durability over time of alkyd resin coating using nano $CaCO_3$. By using nano $CaCO_3$ to replace $CaCO_3$, it will bring better properties for paint film such as gloss, flexural, durability of the paint film. The improvement of the properties of paint films to make it better has been studied and published.

The purpose of this study is to use small-sized materials to replace large particle size coatings in the coatings of alkyd paint film to enhance the advantages of small particle size for better properties for paint film. We have replaced the large particle size $CaCO_3$ powder with nano-sized $CaCO_3$ powder coating to increase the value of paint such as gloss, impact resistance, and durability over time of the paint film. Studying the effects of replacing $CaCO_3$ powder with nano $CaCO_3$ coating in alkyd paint to protect valuable metal surfaces is to increase the gloss, impact, adhesion, and durability of paint film, especially the durability of the paint film over time. The durability of the paint film over time is the most important characteristic of paint because it extends the life of subjects that use this paint to protect metal surfaces.

2 Material and Methods

2.1 Materials

Alkyd- CR 1486-70 DT: Acid index (mg KOH / g solid) 5 – 12, solid content 70 ± 1%, used in paint. Made in Indonesia.

Nano $CaCO_3$: Place of origin is Fujian China, model number NCC-112, the fineness of 50-80 nm. Nanometer calcium carbonate NCC-112 is a material used in the paint industry, with the advantages of fine, uniform, high whiteness and good optical performance. In the paint, NCC-112 has high-density suspension and anti-deposition effect.

$CaCO_3$: Made in Vietnam. $CaCO_3$ content 98%, density 2.7, the iron content of 0.05%, fineness of 10 μm, used for painting.

Bentone 34: Bentone 34, also called montmorillonite, is a special clay mineral, it is a sodium-aluminum hydrosilicate. Bentone 34 which is a term used to refer to natural stone, is a very fine particle material mainly consists of clay minerals. Made in China.

Airex 900: It breaks down the foam formed during mixing, crushing or coating processes to make the film smooth. Made in China.

Dispersant Disper 710s: It is a highly effective dispersant that can disperse organic and inorganic additives in paint to create gloss for paint film. Made in China.

Oct Co: Cobalt octoate 10% is a metal salt used as a drying agent for oil paint systems. The appearance is purple liquid, clear, 55-65% of solid content, metallic content 9.8 - 10.2, density 0.93 - 1.03 g/ml. Made in Dura (India).

Oct Pb: Name of lead octoate product (Pb 32%). Lead octoate is a surface desiccant that hardens the entire surface by drying out the entire film agent, which is often combined with Cobalt and Calcium octoate. Liquid, clear yellow color, solid content 62-72%, Pb content 32 $\pm$ 0.2%. Density 1.2-1.3 g/ml. Application as a drying agent for paints. Made in Thailan.

Oct Ca: Calcium octoate 10% from Maldeep - India. Calcium octoate is a high purity liquid drying agent with strong activity and compatibility. Calcium Octoate is used when combined with Lead and Cobalt octoate, mainly in Alkyd paint.

Xylene solvents: Xylene is a transparent colorless liquid with a pleasant aroma. Chemical formula C_6H_4 (CH_3) $_2$. Density at 20^{o}C is 0.865-0.875 kg/L. Xylene consists of 3 isomers of dimethylbenzene. This mixture is liquid, colorless, often used as a solvent. Made in China.

2.2 Experimental method

2.2.1 Creating of paint samples

Table 1. Composition of paint samples

No	Raw materials	Uses	Formula 1 Wt.% Ratio	Formula 2 Wt.% Ratio	Formula 3 Wt.% Ratio	Formula 4 Wt.% Ratio	Formula 5 Wt.% Ratio	Formula 6 Wt.% Ratio	Formula 7 Wt.% Ratio
1	Alkyd- CR 1486-70 DT	Resin membrane adhesion substance for paint	42	42	42	42	42	42	42
2	Nano CaCO3	Covered substance		1	2	4	8	16	26
3	CaCO3	Covered substance	26	25	24	22	18	8	
4	Bentone 34	Anti-settling substance	0.4	0.4	0.4	0.4	0.4	0.4	0.4
5	Airex 900	Foam breaking substance	0.1	0.1	0.1	0.1	0.1	0.1	0.1
6	Disper 710S	Dispersant substance	0.5	0.5	0.5	0.5	0.5	0.5	0.5
7	Oct Co	Drying substance	0.1	0.1	0.1	0.1	0.1	0.1	0.1
8	Oct Pb	Drying substance	0.2	0.2	0.2	0.2	0.2	0.2	0.2
9	Oct Ca	Drying substance	0.1	0.1	0.1	0.1	0.1	0.1	0.1
10	Xylen	Solvent	30.6	30.6	30.6	30.6	30.6	30.6	30.6
	Total		100	100	100	100	100	100	100

Formula 1

Step 1: Dissolve 4 gams anti-settling additives Bentonite, 1 gam foam breaking agents Airex 900, 5 grams dispersants to disperse 710S in 50 grams of xylene solvents.

Step 2: Dissolve the drying additives 1 gams Oct Co, 2 grams Oct Pb, 1 gam Oct Ca in 50 grams of xylene solvent.

Step 3: Dissolve 420 grams of Alkyd-CR 1486-70 film forming agent in 206 grams of xylene solvent in a 3-liter agitator adjusted at 25 rpm.

Step 4: Slowly add 260 grams of powder coated with $CaCO_3$ to the film-forming resin solution dissolved in xylene

Step 5: Add the dissolved mixture in step 1 and step 2 and stir for another 45 minutes.

Step 6: Crushed by ball grinding equipment for 180 minutes.

Formula 2, 3, 4, 5, 6, 7: Proceed similarly to formula 1 and replace $CaCO_3$ by nano $CaCO_3$ in proportion to the formula. All of the paint formulations were performed under the same conditions, but differ only in the rate of replacing $CaCO_3$ coating materials by $CaCO_3$ nanomaterials then coating on the metal tin sheets to evaluate the quality indicators.

2.2.2 Creating paint coatings

To evaluate the effectiveness of $CaCO_3$ nanomaterials for metal protective coatings, we use the method of comparing the properties of paint when replacing $CaCO_3$ nano-coating by $CaCO_3$ at other rates in the same condition. Each paint formulation was applied to 15 metal tin plates 100x150 mm, 0.5 mm thick with the same coating thickness. From the experimental data, the results are compared to each other to draw conclusions, assess the superiority of using nanomaterials.

Creating a uniform thickness paint is relatively difficult, so we create many models to choose from. There are many tools for creating paint coatings, such as paintbrushes, rollers, spray equipment, manual and automatic film-drawing rulers, etc. The common tool for creating laboratory coatings is a manual paint film ruler. Currently, there are many types of manual paint film ruler, it creates paint film based on the method of creating Doctor Blade technique. We use the manual pull ruler model BGD 201/5 with a 100 μm scale from the Biuged manufacturer. The manual paint film ruler Biuged is made of stainless steel with an accuracy of 2%, easy to use and create relatively uniform paint film. The metal plates used for testing are weighed before coating and after coating 24 hours to determine the amount of coating on the surface. Choose metal tin sheets with the same amount of coating (error of 2%) to determine the index of the paint film.

2.3 Methods of analysis

There are many quality standards related to the quality of paint film, we only analyze some basic properties such as Surface drying time (minutes), Natural drying time (hours), Impact level (kg.cm), Coverage of dry paint film (g/m2), Glossy 60^0, Glossy 85^0 and adhesion of the paint formula over time to evaluate the effectiveness of partial replacement of $CaCO_3$ with Nano $CaCO_3$ and to protect metal surfaces**.** Each paint formulation was applied to 15 metal tin plates 100x150 mm, 0.5 mm thick with the same coating thickness.

Methods of analyzing properties of paint films based on Vietnamese standards used to measure the properties of paint films. Time for paint drying is determined according to Vietnam standard TCVN 2096-1: 2015[(10)]. Gloss 60^0, 85^0 determined according to TCVN 2101 – 1993[(11)]. Impact level determined according to TCVN 2100-2: 2007[(12)]. Coverage of dry paint film TCVN 2095: 1993[(13)]. The standard of adhesion for the paint formula over time is the most important for determining the durability of paint films. We use the method of cross-cut tests for the determination of adhesion according to TCVN 2097: 1993[(14)].

3 Results and discussion

3.1 Properties of paint samples

Table 2. Properties of paint samples

No	Properties	Formula 1	Formula 2	Formula 3	Formula 4	Formula 5	Formula 6	Formula 7
1	Surface drying time (minutes)	33	32	31	29	26	25	24
2	Natural drying time (hours)	20	19	18	17	16	15	15
3	Impact level (kg.cm)	70	71	73	75	77	78	79
4	Coverage of dry paint film g / m2	83	83	83	83	83	83	83
5	Glossy 60°	89	90	92	94	96	97	98
6	Glossy 85°	87	88	90	92	93	94	95

From the data shown in Table 2 the impact level increases when replacing $CaCO_3$ coating with $CaCO_3$ nanomaterials, the higher the replacement rate, the faster the impact increases, the impact increased by about 13% (70 to 79 kg.cm).

The gloss of 60° and 85° are increased when replacing $CaCO_3$ coating with $CaCO_3$ nanomaterials with a higher replacement rate, the glossiness also increases faster, glossy 60° increased by about 10%, glossy 85° increased by about 9%. This can be explained by the fact that the $CaCO_3$ nano-coating is very small and smooth, so it gives a gloss on the metal surface. Therefore, the finer the material, the more glossy metal surface. When the material is nm-sized, the number of atoms on the surface will be a significant proportion of the total number of atoms. Therefore, the effects related to the surface, or the surface effect, will become important, making the properties of materials with nanometer dimensions different from materials in bulk.

3.2 The change of adhesion over time

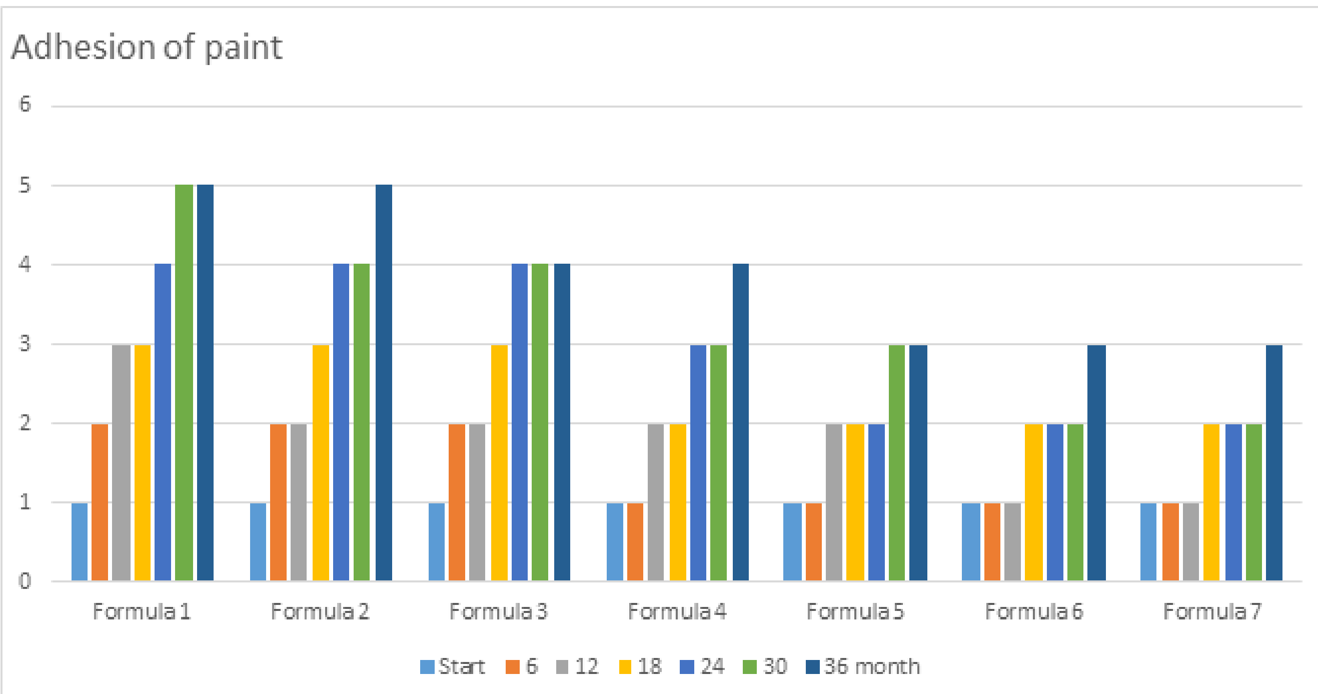

Fig 1. The change in the adhesion of the paint formula over time

The data in Figure 1 shows the adhesion of paint formulas varies with time. The higher ratio of using nano-coating materials, the less change in adhesion. It means that it is more durable, the life of the paint film is higher when using $CaCO_3$ nanocoating material, the durability of paint film over time nearly doubled when completely replacing the $CaCO_3$ coating with $CaCO_3$ nanomaterials. This can be explained by the fact that the metal surface structure is not smooth and ideal, but from a micro perspective, it is also rough with very small slots, holes that make the coating of different sizes permeate deep into the surface at different levels. Due to the size of nano $CaCO_3$, very small from 50-80 nm, it easily penetrates to the metal surface, so the adhesion force between the coating and metal surface is better than the adhesion force of $CaCO_3$ coating because nano $CaCO_3$ material makes the paint more durable and prolong the life of the coating.

Experiments show that partial replacement of $CaCO_3$ with Nano $CaCO_3$ to protect metal surfaces has brought better results for paint film properties such as gloss, impact resistance, and especially service life of paint film over time. Paints with nano calcium carbonate have many good properties such as high gloss, easy to spread and resistance to weather conditions, improved corrosion resistance properties, against environmental impacts such as moisture, ultraviolet rays. Because $CaCO_3$ nanomaterials are more expensive than $CaCO_3$ coatings, the replacement should only be applied on a case by case basis. Metal surfaces of ordinary, inexpensive objects, tools, equipment if using alkyd paint with nano $CaCO_3$ coating need to be considered economically because this type of paint is more expensive than that used with powder coatings $CaCO_3$, so in practice, they should only replace less than 8% by weight. However, in cases that require good paint film quality, high gloss and, durability over time for metal surfaces of valuable tools and equipment, the paint with nano-coating $CaCO_3$ is very suitable.

4 Conclusion

The novelty of the study is replacing $CaCO_3$ coating material with nano $CaCO_3$ and confirms the effectiveness of nanomaterials. Replacing $CaCO_3$ by nano $CaCO_3$ in alkyd resin for metal paint has increased the adhesion of $CaCO_3$ coating to the metal surface, which makes the film glossier, the better impact resistance of paint film and the life of the paint film is more durable under the impact of the environment. Therefore, nano-material $CaCO_3$ is a good coating in alkyd resin for metal paint, it improves the properties of paint film better than $CaCO_3$ material.

$CaCO_3$ nanomaterials are much more expensive than $CaCO_3$ so in practice they should only replace less than 8% by weight, the higher the rate of replacing $CaCO_3$ materials with $CaCO_3$ nano, the better the properties of the paint film, so paint manufacturers should choose the replacement rate suitable for the purpose of the paint film quality.

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Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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