Formulation of Heat Resistant Paint from Palm Oil Based Resin by Using Nano-Silica Particles

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Abstract

Paint is the main choices of coatings for various materials, machinery and buildings. Paints formulated from renewable resources and non-toxic chemicals are in demand. The objective of this study is to prepare and characterize heat resistant paint from palm oil based resin by using nano-silica particles. Palm oil based paint was formulated using resin prepared from cooking oil waste, varied amount of nano-ceramics particles and fixed amount of pigment. Painted samples of aluminium sheet were prepared from formulated paint, cured oven heating method. Heat resistance and corrosion resistance were performed. Sample containing 0.6% silica showed best performance under heat no visible cracks even at 140 °C. Tafel plot shows corrosion resistance with Ecorr -0.91479 V, Icorr 3.2X10^-6 A, Corrosion rate 0.0328216 mmy. The best formulation of paint can be benefited in many areas such as industrial paint industry, household appliances that required high thermal resistant and eco-friendly paint.

Keywords: paint; heat resistant; nano-silicas particles;
1. Introduction

Paint is one of the oldest synthetic substances known, with a history stretching back into prehistoric times. It was made more than 35,000 years ago by prehistoric man as they mixed clay and chalks with animal fats and used these paints to depict their hunts on cave walls. By 2500 BC the Egyptians had improved the technology considerably. The technology improved further during the first millennium BC then lapsed for many years, with techniques being passed down from generation to generation [1]. Now in the twentieth century, the chemistry of many aspects of paint manufacture and function are already been taken account, meaning that paint manufacture has finally progressed from being an art to being a science. The main raw materials used in the formulation of paint are solvent, pigment, binders and additives. The chemical composition of paint varies depending on the desired paint properties. Alkyd resins are thermoplastic polyester resins made by heating polyhydric alcohols with polybasic acids or their anhydrides. They are used in making protective coatings with good weathering properties and are important ingredients in many synthetic paints due to their versatility and low cost [2]. A lot of researches are being developed searching for improvement of the coatings properties and the reduction of the costs, modifying the resin components and the synthetic method.

Ceramic coatings are well known for the heat resistance properties in fact some of the highest heat coatings available are ceramics. It also provides corrosion protection and chemical resistance and a hard finish. By applying high temperature ceramic coating insulation, the metal underneath the paint film also can be protected [3].
The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. The nano-composites find their use in various applications because of the improvements in the properties over the simpler structures. Few of such advantages are improved mechanical properties such as strength, modulus and dimensional stability, higher thermal stability and heat distortion temperature. Furthermore, at elevated temperatures, the material must exhibit high resistance to thermal shock, oxidation, and subcritical crack growth. Ceramic nano-composites have been shown to be extremely important for such applications.

The demand for enhanced scratch and wear resistance in today’s clear and pigmented coatings is increasing. The idea of an everlasting surface that retains its initial properties is the driving force for the ongoing research in this field [4].

Settling time, quick curing time, thermal insulation and thermal barrier property and hardness of a paint are among the crucial characteristics to produce a good paint. Apart from the composition, thickness of the coating, environmental conditions play a crucial role. Out of the weathering conditions, humidity and temperature are the lead players in formulation of paint [5, 6, 7]. Therefore, high resistant paint is one of the main factors in paint formulation and evaluation of the performance of paint on metal substrate is a good way to measure the optimum formulation of paint. Therefore, this research aims to study the percentage of nano-ceramic particles for the enhancing of heat resistance properties, determination of the optimum dispersion of additives into resin, solvent and pigments, determination of curing time of paint and evaluation of thermal resistant property, corrosion resistance and heat flow on paint.
2. Materials and Method

Palm oil based alkyd resin prepared from waste cooking oil, alkyd resin (34% oil length, acid value < 10mgKOH/g) obtained from supplier Sunny, styrene (C₈H₈, 99%), toluene (C₇H₈, 99%), acetone ((CH₃)₂CO, 99%), sodium hydroxide (NaOH, 99%) sodium chloride (NaCl, 99%) and hydrochloric acid (HCl, 37%), zinc oxide (ZnO, 99%) used as pigment, nano silica (SiO₂) as the additives, benzoyl peroxide(C₁₄H₁₀O₄) used as initiator, cobaltous (II) napthenate (CoC₂₂H₄₄O₄, 99%) used as catalyst, aluminium substrate were used in this study.

2.1 Preparation of paint

5 grams of alkyd resin was dissolved in 5 grams of palm oil based alkyd resin. This mixed alkyd resin was used as binder to formulate paint with different composition of nano silica. The fixed percentage composition of solvent is 40%, binder is 30 % and pigments is 25%. The actual composition used to formulate the paint are tabulated as in Table 2.1. Nano silica was dispersed in 10 ml of acetone to obtain a solution by mechanical stirring for 30 minutes. Alkyd resin (binder), toluene (solvent), zinc oxide (pigment) and nano silica were dispersed by the aid of mechanical stirring until a homogenous mixture obtained. 2 drops of Cobaltous (II) napthenate a catalyst and 2 drops of butyl peroxide were added and stirred for another 10 minutes.

| Samples | Toluene (ml) | Silica (gram) | Resin (gram) | Zinc oxide (gram) |
|---------|-------------|--------------|--------------|------------------|
| 1       | 4.5         | 0.02         | 3.00         | 2.50             |
| 2       | 4.5         | 0.04         | 3.00         | 2.50             |
| 3       | 4.4         | 0.06         | 3.00         | 2.50             |
| 4       | 4.4         | 0.08         | 3.00         | 2.50             |
| 5       | 4.4         | 0.10         | 3.00         | 2.50             |
2.2 Curing process of paint

Paint was cured by putting the paint in a drying paint oven at 105°C and checked frequently for the dryness by using the finger-tip. The time for curing was recorded as drying or curing time of the paint.

2.3 Performance evaluation on paint

Heat resistant test, corrosion resistance test and Differential Scanning Calorimetry (DSC) analysis will be performed on five samples of paint.

(i) Heat Resistant Test

This test was performed on metal substrate coated with layers of paint applying heat onto the surface by putting the samples in drying oven for a period of time with increasing temperature (from 60°C to 140°C) for all the samples. Surfaces of metal substrate were observed for every 2 hours.

(ii) Corrosion Resistance Test

Metal substrate coated with layer of paints were immersed in several solutions viz., distilled water, 5% sodium hydroxide solution, 5% sodium chloride solution and 1M hydrochloric solution. The weight of each samples were weighed before been immersed and after 2 weeks, the weight of the samples were taken. Besides these Tafel plot was taken from potentiostat in 3.5%NaCl solution using three electrode system where platinum wire was counter electrode and Ag/AgCl was reference electrode. Frequency range was $10^{-1}$Hz and $10^{5}$Hz, AC amplitude was 20 mV, scan rate was 1mV$^{-1}$ and scanning range was -300mV to 300mV (Open circuit potential).

3. Result and Discussion

3.1 Curing Time
Table 3.1: Drying time of paint

| Time/minutes | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|--------------|----------|----------|----------|----------|----------|
| 30           | Not dry  | Not dry  | Not dry  | Not dry  | Not dry  |
| 60           | Not dry  | Not dry  | Not dry  | Not dry  | Not dry  |
| 90           | Not dry  | Not dry  | Not dry  | Not dry  | Not dry  |
| 120          | Not dry  | Not dry  | Not dry  | Not dry  | Not dry  |
| 150          | Not dry  | Not dry  | Not dry  | Not dry  | Not dry  |
| 180          | Not dry  | Not dry  | Not dry  | Not dry  | Not dry  |
| 210          | Not dry  | Not dry  | Not dry  | Not dry  | Not dry  |
| 240          | Not dry  | Not dry  | Not dry  | Not dry  | Not dry  |
| 270          | Dry      | Dry      | Dry      | Dry      | Dry      |

Table 3.1 shows that drying time for all paint samples is 6 and half hours. An organic peroxide initiator, butyl peroxide is used as radical initiators to induce chain-growth polymerization reactions. In this formulation of paint, cobaltous (II) napthenate which is the metal complex primary drier for alkyd paints is used as an autoxidation catalyst thus speed up the curing time of paint [2,8]. Initiator and catalyst both contribute in the speed up process of polymerization and curing time of the paint.

3.2 Heat Resistant Test

Table 3.2 shows the results of heat resistant test at different temperature (60,80,100,120 and 140°C). No visible crack on the surface was found indicates durability and high thermal resistant at elevated temperature. The colour of the samples that has been exposed to high temperature in the oven tend to turn yellowish. This is because at elevated temperature thermochromism happens which is problematic for plastic, coating and textile applications [9].

Table 3.2: Effect of temperature on painted aluminium substrate

| Samples | 60°C   | 80°C   | 100°C  | 120°C  | 140°C  |
|---------|--------|--------|--------|--------|--------|
| 1       | No crack | No crack | No crack | No crack | No crack |
| 2       | No crack | No crack | No crack | No crack | No crack |
| 3       | No crack | No crack | No crack | No crack | No crack |
| 4       | No crack | No crack | No crack | No crack | No crack |
| 5       | No crack | No crack | No crack | No crack | No crack |
Table 3.3 shows no crack found on the surface of the samples from the heat exposure under the sun at 2 days interval for 10 days period of time.

| Samples | 2 days | 4 days | 6 days | 8 days | 10 days |
|---------|--------|--------|--------|--------|---------|
| 1       | No crack | No crack | No crack | No crack | No crack |
| 2       | No crack | No crack | No crack | No crack | No crack |
| 3       | No crack | No crack | No crack | No crack | No crack |
| 4       | No crack | No crack | No crack | No crack | No crack |
| 5       | No crack | No crack | No crack | No crack | No crack |

3.3 Corrosion Resistance Test

After the samples are immersed in distilled water (neutral solution), 5% aqueous sodium hydroxide solution (alkaline solution), 5% aqueous sodium chloride solution (saline solution) and 1M aqueous hydrochloric acid solution for 2 weeks at room temperature 28-30ºC, the percentage of weight difference of aluminium substrate of before and after immersion are recorded as below in Table 3.4.

| Solution                  | Sample | Weight Before (grams) | Weight After (grams) | Percentage of Weight loss (%) |
|---------------------------|--------|------------------------|----------------------|-------------------------------|
| Distilled water           | 1      | 0.166                  | 0.163                | 0.3                           |
|                           | 2      | 0.176                  | 0.173                | 0.3                           |
|                           | 3      | 0.158                  | 0.158                | 0                             |
|                           | 4      | 0.176                  | 0.174                | 0.2                           |
|                           | 5      | 0.168                  | 0.166                | 0.2                           |
| 5% Sodium Hydroxide (NaOH) solution | 1      | 0.173                  | 0.105                | 6.8                           |
|                           | 2      | 0.192                  | 0.137                | 5.5                           |
|                           | 3      | 0.171                  | 0.139                | 3.2                           |
|                           | 4      | 0.149                  | 0.142                | 0.7                           |
|                           | 5      | 0.178                  | 0.177                | 0.05                          |
| 1                         | 0.143  | 0.137                  | 0.6                  |
From the table above, the average percentage of weight loss in distilled water is insignificant 0.2% where as in distilled water, 5% aqueous sodium hydroxide solution Sample 1 has the highest percentage of weight loss. In 5% aqueous sodium chloride solution and 1M aqueous hydrochloric acid solution Sample 5 losses most weight. Table 4.7 indicates that the samples are highly resistant to distilled water and aqueous NaCl salt solution and have poor resistant to aqueous NaOH solution and dilute HCl acid. This poor alkali resistance of resins is due to the presence of alkali hydrolyzable ester group [10].

**Figure 1:** Immediate Condition of aluminium substrate coated with paint immersed in different solutions
Figure 2 shows that after 2 weeks, the samples painted aluminium substrates resist well in distilled water and aqueous NaCl salt solution where as don’t have sufficient resistance in HCl and NaOH solution.

Figure 3 shows the tafel plot of paint containing nanosilica. Using Nova 2.1.4 software various corrosion parameter were measured as $E_{corr} = -0.91497V$, $I_{corr} = 3.288 \times 10^{-6} A$ and Corrosion rate = 0.038216 mm/year. These value indicate a higher corrosion resistance.[11]
Figure 3: Tafel plot of silica nanoparticle filled paint sample.

4 Conclusion
A good formulation of paint has to be well dispersed and obtained a homogenous mixture after the mixing process. The curing time of all samples are 270 minutes and all of the samples has no visible crack on the surface after been subjected under high temperature condition as well as been exposed to direct sunlight. There are slight changes in term of colour for all of the samples that are been exposed to high temperature. Based on the results obtained and after the analysis, it is concluded that sample containing 0.6% nano silica is less vulnerable to heat as well as corrosion.

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References

[1] NPCS Board 2013. Manufacture of Paint, Vanish and Allied Products. 2nd revised edition. Delhi, India. NIIR Project Consultancy Services.

[2] Li, D., Lin, C., Batchelor-McAuley, C., Chen, L., Compton, R.G., 2018. Tafel analysis in practice. *Journal of Electroanalytical Chemistry* **826**, 117-124.

[3] Huang, K., Hou, C., Hu, B., Li, Y., Chen, L., 2012. Preparation and property analysis of a heat-resistant and anti-eroding coating. *Procedia Engineering* **27**, 1228-1232.

[4] Favache, A., Daniel, A., Teillet, A., Pardoen, T., 2019. Performance indices and selection of thin hard coatings on soft substrates for indentation and scratch resistance. *Materials & Design* **176**, 107827.

[5] Ashby, M., Johnson, K., 2010. *The Stuff... Multi-Dimensional Materials*, in: Ashby, M., Johnson, K. (Eds.), *Materials and Design* (Second Edition). Butterworth-Heinemann, Oxford, Chapter 4 pp 54-93.

[6] Yang, S., Cui, Z., Zhang, Y., Jiang, T., Yang, Q., Sun, Y., 2019. Photosynthetic pigments in surface sediments in the northwest of the Bohai Sea, China: Potential implications for sediment deposition of brown tides of *Aureococcus anophagefferens* in coastal waters. *Ecological Indicators* **102**, 145-153.

[7] O'Connor, D., Hou, D., Ye, J., Zhang, Y., Ok, Y.S., Song, Y., Coulon, F., Peng, T., Tian, L., 2018. Lead-based paint remains a major public health concern: A critical review of global production, trade, use, exposure, health risk, and implications. *Environment International* **121**, 85-101.

[8] van Gorkum, R., Bouwman, E., 2005. The oxidative drying of alkyd paint catalysed by metal complexes. *Coordination Chemistry Reviews* **249**, 1709-1728.

[9] Tang, P., Liu, Y., Liu, Y., Meng, H., Liu, Z., Li, K., Wu, D., 2019. Thermochromism-induced temperature self-regulation and alternating photothermal nanohelix clusters for synergistic tumor chemo/photothermal therapy. *Biomaterials* **188**, 12-23.

[10] Mahapatra, S.S., Karak, N., 2004. Synthesis and characterization of polyesteramide resins from Nahar seed oil for surface coating applications. *Progress in Organic Coatings* **51**, 103-108.
[11] Li, D., Lin, C., Batchelor-McAuley, C., Chen, L., Compton, R.G., 2018. Tafel analysis in practice. *Journal of Electroanalytical Chemistry* **826**, 117-124.