Volume-2, Issue-5, September-2018: 39-48
International Journal of Recent Innovations in Academic Research **ISSN: 2635-3040**

Formulation of Emulsion Paint from the Copolymer Composite of Polyvinyl Acetate/ Hydroxylated Neem Seed Oil (PVAC/HNSO)

[1]Saljaba, G.M., [2]Archibong, C.S., [3]Aminu, A. and [4]Osemeahon, S.A.

[1]Department of Chemistry, College of Education Waka-Biu, Borno State, Nigeria
[2]Department of Chemical Sciences, Federal University Wukari, Nigeria
[3]Department of Chemistry, Federal College of Education Yola, Adamawa State, Nigeria
[4]Department of Chemistry, Modibbo Adama University of Technology, Yola, Nigeria

Abstract: Modification of polyvinyl acetate (PVAC) with hydroxylated neem seed oil (HNSO) to form emulsion paint composite (HNSO/PVAC) was undertaken in this work. The characterization of the physico-chemical properties of the copolymer resin, place side by side with the conventional paint binder polyvinyl acetate (PVAC), revealed that the composite shows a significant improvement in those parameters that have hampered the full utilization of polyvinyl acetate as a binder in the coating industry (these parameters include, hardness, brittleness and poor water resistance). The synthesized composite HNSO/PVAC and conventional PVAC binder were separately subjected to Standard emulsion paint formulation and method of production, analytical parameters of the individually prepared paint were compared. The viscosities, density, refractive index, melting point, moisture uptake, were all within the range of other paints. Hydroxylated neem seed oil modified polyvinyl acetate paints show no sign of leaching and phase separation even after 12 months showing good compatibility of the Hydroxylated neem seed oil and polyvinyl acetate.

Keywords: Polyvinyl acetate, Hydroxylated neem seed oil, Emulsion paint, Copolymer, composite

Citation: Saljaba, G.M., Archibong, C.S., Aminu, A. and Osemeahon, S.A. 2018. Formulation of Emulsion Paint from the Copolymer Composite of Polyvinyl Acetate/ Hydroxylated Neem Seed Oil (PVAC/HNSO). International Journal of Recent Innovations in Academic Research, 2(5): 39-48.

Introduction

The amalgamation of organic and organic functionalities into a single polymer offers a unique combination of distinctive properties of both constituents viz reduction in the emission of volatile organic compound, good process ability, improved toughness, flexibility, chemical resistance and some other properties like weather ability, UV resistance and thermo oxidative stability, etc. The adoption of such amalgamation has become a sign qua non, especially with the environmental demands that have led to nationwide programme to limit volatile organic compounds (VOCs). Recent research developments using chemical design to achieve pollution prevention have resulted in totally new synthetic routes which eliminates standard feedstocks. Well known reactions, such as the Friedel-Craft reaction, are now being investigated to find alternatives as replacement and so is the coating industries not left out in the move towards the production of solvent less based coatings instead of the organic solvent based coatings that emits VOCs (Shangde *et al*,. 2011).

In the constituents for production of solvent less paint, PVAC binder usually takes between 17 to 33% total cost of production depending on paint type and this raw material is not available locally, therefore imported (Huntsman, 2013). Hence, high cost of this raw material (binder) and consequently high cost of production due to the use of expensive binder. In addition, PVAC is hard and brittle, has poor water resistance and non-biodegradability which can contaminate the environment if not properly handled. Outside the production of paint PVAC emulsions are also used as adhesives for porous materials, particularly for wood, paper, and cloth, and as a consolidate for porous building stone, in particular sandstone (Surajudeen and Zebulu, 2015), hence, the need to improve on its qualities. Vegetable oil represents one of the cheapest and most abundant biological feedstock available. Its use as blending tools offers numerous advantages such as low toxicity, gloss and inherent biodegradability. The double bonds in the vegetable oil are used as reactive sites in coatings and they can also be functionalized by epoxidation (Osemeahon and Archibong, 2011).

Neem seed oil a typical vegetable oil, will impart valuable properties to the coating but in order to furnish these properties, the oil must be incorporated into the formulation, this can be achieved by first hydroxylating the already epoxidized neem seed oil to create OH bonding sites to enable proper blending. The main advantages of using this neem seed oil is that the need for traditional solvent as white spirit can be effectively eliminated which will leads to the following benefits: Zero volatile organic content, Eliminate healthy risk associated with solvent in respiratory systems. Environmental friendly, solvent free and 100% biodegradable in nature, Brushes and other equipment can be easily cleaned with water, minimize fire risk (Ezeagba *et al.*, 2014). Once the above is successfully done, physical and chemical interaction will then be possible, the OH functional groups in the hydroxylated neem seed oil will combine with the hydrogen groups in the polyvinyl acetate by condensation processes, the composite HNSO/PVAC will be form and water is eliminated. Therefore, the aim of this research is to formulate an emulsion paint using this synthesized composite and then compared with emulsion paint produced from conventional paint binder (PVAC).

Materials and Methods

Materials

The materials used were PVA, Neem seed oil, NaOH, HCl, Sodium dihydrogen phosphate, Sulphuric acid, Acetic acid, Formic acid, Hydrogen peroxide, Ammonium hydroxide and Butanol are analytical grades (i.e. products from the British Drug House, BDH). Anti-foam, Aluminium silicate, Calgon, Kaolin, Antiskining agent, Sodium carbonate, Calcium carbonate, Troysan, Titanium dioxide, Genepour, Drier, and Bermocoil. All materials were used as received. PVAC was bought from Jimeta market, Adamawa State, Nigeria.

Methods

Preparation of Hydroxylation Neem Seed Oil

The hydroxylation reaction was performed in a 1000 cm^3 three neck flask equipped with a reflux condenser and a thermocouple. The flask was placed on a hot plate with temperature control. 150 cm^3 of the epoxidized neem seed oil was hydroxylated using alcohol (methanol and isopropanol) with a molar ratio of 4:1 to the oil and water at a molar ratio of 2:1 was mixed with the epoxidized oil and sulphuric acid catalyst in the reactor. The reaction was performed at a fixed temperature of 60°C for 5 hours. Uniformity was maintained using a magnetic stirrer which runs at about 1600 rpm (Petrovic *et al.,* 2002). The product was then cooled and decanted in order to separate the organic-soluble compounds from water-soluble ones. The product was washed with warm water (in small aliquots) in order to remove residual contaminants. The procedure was repeated 3 times.

Preparation of NSO/PVA Blends and Films

Blend of HNSO/PVAC was prepared by adding varying amount of HNSO in PVAC resin. The mixture was stirred and left for 24 h at room temperature (30°C) and then poured into a glass Petri dish for casting. The resin was also allowed to cure and set for seven days at (30°C). The physical properties of the resin films were investigated using the method as explain by (Osemeahon *et al.,* 2010).

Determination of Viscosity and Gel Time

The standard method of viscosity determination was employed using the viscometer bath capillary inserted into the viscometer bath. A 15 ml of the resin was measured and poured into the U-tube viscometer with capillary and then corked. The U-tube was suspended into the viscometer bath containing water and the temperature of the bath was 33°C. The cork was removed and the time taken for the content to run up starting from the top mark to the middle mark was noted using a stop watch. From this result the viscosity of the sample was calculated. Three different readings were taken for each sample and the average value calculated. Determination of the gel point of the resin was done by monitoring the viscosity of the resin with time until a constant viscosity profile was obtained (Osemeahon *et al.,* 2010).

Determination of Density, Turbidity, Melting Point and Refractive Index

The mettle Toledo XS 64 was used in determining the density of the cured resin via Archimedes principle, three readings were taken for each sample and average values were calculated**.**

Determination of Turbidity

The turbidity of the resin samples was determined by using Hanna microprocessor turbidity meter (Model, H193703). Determination of the melting points of the film samples was done using Galenkamp melting point apparatus (Model, MFB600-010F). The refractive indices of the resin samples were determined with Abbe refractometer. The above properties were determined according to standard methods (AOAC, 2000).

Determination of Moisture Uptake

The classic laboratory method of measuring high level moisture of solid or semi-solid material loss on drying (LOS) was adopted. In this technique a sample of material is weighed, heated in an oven for an appropriate period, cooled in dry atmosphere of a desiccator and then reweighed. The difference between the weighed and the reweighed sample were then recorded as the moisture intake by the resin. Triplicate determinations were made for each sample and mean value recorded**.**

Elongation at Break

The elongation at break was measured using Inston Tensile Testing Machine (Model 1026). Resin films of dimension 50 mm long, 10 mm wide and 0.15 mm thick was brought to rapture at a clamp rate of 20 mm/min and a full load of 20 kg. A number of five runs were carried out (Dimas *et al*., 2013).

Water Solubility

The solubility of blend in water was obtained by mixing 1 ml of the resin with 5 ml of distilled water at room temperature (30°C) (Dimas *et al*., 2013).

Paint Formulation

The method described by Karakas *et al*., (2011) was adopted for the paint formulation. The method splits the production process into three main stages as shown in table 1.

Table 1. Recipe for the Formulation of Emulsion Paints From PVAC and HNSO/PVAC Binders

Stage	**Materials**	**Quantity (grams)**
First	Water	185.00
	Anti-foam	0.20
	Drier	0.20
	Calgon	1.16
	Genepour	1.16
	Bermocoill	2.50
	Tryostan	1.14
	Dispersant	0.20
	Butanol	5.00
	Ammonia	0.54
Second (Mill base)	TiO_2	50.00
	Al_2SiO_3	11.20
	Na_2CO_3	0.58
	Kaolin	2.52
	$CaCO_3$	123.00
Third (Letdown)	Binder	100.00
	Water	15.00
	Dispersant	0.20
	Nicofoam	0.20
	Anti-skining agent	0.20
Total		500

Paint Samples Test Procedures

The methods of Standard Organization of Nigeria (SON) was adopted in the analysis of the paint samples.

Determination of Viscosity

Determination of Viscosity of Emulsion Paints at ±270C (NIS, 1990). The paint sample was poured into a sample can to a level of about 2.5 cm from the top of the can. The can was then placed on the turntable of the rotothinner after it had been switched on. The disc was immersed into the emulsion paint inside the sample can. The disc was allowed to rotate inside the paint sample until the peak viscosity value was obtained. The viscosity reading was taken from the graduated scale around the turntable. The disc was raised and the sample can removed, following which the disc was thoroughly cleaned with a brush and water.

pH Measurement and Opacity Test

The pH of paint sample was determined by using phywe pH meter model 18 195.04.The paint sample was scooped with a palate knife and spread evenly across the width of a Morest chart (black and white striped paper) about 4 cm from the edge of the paper. The paint was then evenly applied down the length of the paper by means of the K-bar (stainless steel bar) and left to dry. A second coat was applied using the same application technique but with a space of 5 cm left from the edge of the first coat. The opacity was assessed by the extent to which the black and white stripes were covered by the paint. Three determinations were made for each sample and mean value recorded for quality assessment.

Drying Time and Flexibility

Dry time was evaluated by applying the paint sample on a glass panel with the aid of bar applicator, and allowed to dry. Dry to touch was taken when the paint film was no longer sticking to the finger and dry to hard was taken when the film resisted finger print. Triplicate evaluations were made for each sample and mean value assessment recorded. For flexibility test, paint sample was applied on a freshly degreased and chromate aluminium with the aid of paint applicator. The film was allowed to air dry under room temperature (27-30°C) for 7 days. The panel with the film was bent through 180° with a smooth action (taking 1-2 seconds). The panel was then removed and examined for cracking or loss of adhesion. Any crack or loss of adhesion indicates inflexibility or brittleness. Triplicate determinations were made at 27-30°C for each sample for quality assessment.

Chemical Resistance

The chemical resistance of the paint films was carried out thus; three flexible aluminium panels (150 mm x 0.3) were used as the test panels. A coat of paint with paint applicator was applied on the panels. One litter glass beaker was filled with 0.1 M NaOH solution to a depth of 150 mm and the test pieces was immersed for 48 hours to the depth of approximately 120 mm. The test piece was removed, washed with running water and stand to dry for 2 hours. The above procedure was repeated using 0.1M HCl and 0.1M NaCl respectively. Poor chemical resistance indicated by the presence of any surface defects such as cracking, blistering, peeling or changes in color.

Tackiness

This was carried out qualitatively on the dried film by hand feeling to find out if the paint film is sticky or not. Stickiness of a dried paint film is an indication that the film is tacky. Triplicate samples were used for each determination and the average quality assessment recorded.

Adhesion Property

This was carried out by applying a coat of paint film with film applicator on a degreased metal panel and allowed to dry for 48 hours. Two sets of lines, one crossing perpendicularly over the other were drawn tester on the paint film. An adhesive tape was pressed firmly with the thumb covering all the interactions of the perpendicular line. The adhesive tape was held at its loose ends and forcefully removed from the panel. Removal of more than 50% of the square lines of the paint film indicates a poor adhesion. Triplicate determinations were made 27-30^{o}C for each sample for quality assessment.

Resistance to Blistering

To determine Resistance to blistering, undiluted paint sample was applied to a glass Panel with an applicator to give a wet film thickness of about 120 µm, which was allowed to dry for

24 hours. At the end of this period 4 ml of distilled water in the form of circular drop was placed on the film. The presence of blistering, wrinkling, swelling or cracking within a period of 30 minutes indicates poor water resistance. Triplicate determinations of each sample were made and quality assessment recorded as mean.

Stability Test

The paint sample was fully sealed in a container and allowed to stay at room temperature (27^{o}C) for 12 months. At the end of this incubation period, the sample was re-examine or any change in viscosity or coagulation of the emulsion paint. Absence of coagulation or any change in viscosity is regarded as pass. Triplicate samples were used for each determination and average recorded

Results and Discussion

Table 2 displays some physico-chemical parameters of PVAC and HNSO/PVAC, and also compares the values with the acceptable standards in the coating industry. The densities of both PVA and HNSO/PVAC are within acceptable limits in the coating industry. On a closer look HNSO/PVAC exhibits a lower density and this could be attributed to the changes in the morphology of the composite as a result of the inclusion of the bulky structures of HNSO leading to increase in specific and free volume in the composite (Saadati *et al.,* 2013).

The refractive index of both resin are also within acceptable limit in the coating industry, the high refractive index value of HNSO/PVAC can be attributed to differences in molecular features, molecular orientation depending on morphology and crosslink density (Osemeahon and Barminas, 2007). Reduction in the moisture uptake could be as a result of the introduction of hydrophobic HNSO or as a result of the condensation reaction that occurred due to possible interactions of the OH group of HNSO and hydrogen of PVAC (Osemeahon *et al.,* 2013, Zorba *et al.,* 2008).

The Viscosity of the composite HNSO/PVAC was lower when compared to PVAC, this could be due to decrease in molecular weight and/or a fall in internal friction due to the incorporation of a less bulky polymer into the PVAC binder (Oladipo *et al.*, 2013). The melting point of HNSO experience a dramatic reduction when compared to that of pure PVAC, this of course indicates reduction in hardness and hence a demonstration of the impact of flexibility introduced due the inclusion of flexible HNSO (Yildiz *et al.*, 2007).

Table 2. Comparison of Some Physical Properties of PVAC and HNSO/PVAC Resins

Parameters	**PVA**	**HNSO/PVAc**	**Acceptable Level in the coating industry (Osemeahon *et al.*, 2013).**
Density (g/cm3)	1.59	1.3	1.07 (min.)
Refractive index	1.41	1.431	1.4000 (min.)
Moisture uptake (%)	0.4129	1.14	3.10 (max.)
Viscosity (MM2/S/S)	383.42	146.76	3.11- 38.00
Melting point (0C)	185	176	200(max.)
Turbidity (NTU)	1308	3288	-
Gel time (Min)	88	235	-
Solubility	Soluble	Soluble	-

Some Physical Properties of PVA and HNSO/PVA Paints Samples Developed

Table 3. is a presentation of some properties obtained from paints sample developed. As seen from the table, all the paints formulated from HNSO/PVA and PVA shows good adhesion, tackiness and hardness properties. This behaviour can be due to high molecular weight and hence high crosslink density of both the pure PVAC and HNSO/PVAC binders (Habib and Bajpai, 2011). Properties such as pH, viscosity, flexibility and opacity of both PVAC and HNSO/PVAC fall within the acceptable ranges for paints (SON, 1990).

Both the paints from the PVA and HNSO/PVAc binders passed resistance to blistering test. These results indicate that HNSO segment has been cross linked into the HNSO/PVAc copolymer thereby impacting hydrophobic character. The higher degrees of cross-linking give rise to less free volume and solvent molecules hardly pass through the cross linked network (Osemeahon and Dimas, 2014). This implies that the paint can perform well when exposed to environmental conditions such as rain and sun. The pure PVAc paint failed water resistance test as a result of the inherent property of the resin in addition to low molecular weight of the PVA binder used in the paint formulation (Ayoub *et al.*, 2013; Zorba *et al.*, 2008).

The drying time of PVAc and HNSO/PVAc paints falls outside the specified range (Petrovic The low drying time displayed by PVAc paint is attributed to the low molecular weight and hence low crosslink density of the PVAc binder while the HNSO/PVAc has high crosslinked density due to increased in molecular weight which enhanced drying (Hussain and Nasr, 2010).

Table 3. Some Physical Properties of Paint Formulated From HNSO/PVAC Binders

Parameter	**PVAC**	**HNSO/PVAC paint**	**SON Standard**
pH	7.32	7.58	7-8.5
Viscosity	14.7	14.6	6-15
Flexibility	Pass	Pass	Pass
Opacity	Pass	Pass	Pass
Adhesion	Pass	Pass	Pass
Stability	Pass	Pass	Pass
Tackiness	Pass	Pass	Pass
Resistance to blistering	Pass	Pass	Pass
Water resistance test	Fail	Pass	Pass
Dry time (min)			
Touch	51	53	20
Hard	73	10	120

Table 4 shows the effect of paint in the three medium (HCl; acidic medium, NaOH; alkaline medium, NaCl; salt medium). The ability of a paint to resist chemical attack or staining is one of the desirable qualities of a good coating film. Chemical resistance test determines the ability of a coating film to resist chemical attack. From the results, both PVAc and HNSO/PVAc were unaffected by salt medium. PVAc and HNSO/PVAc film were also unaffected by both the acid and alkalise solutions.

Table 4. Comparison of the Result of Chemical Resistance of PVAC and HNSO/PVAC

	Media		
Sample	**0.1M HCl**	**0.1M NaOH**	**0.1M NaCl**
PAVC	No effect	No effect	No effect
HNSO/PVAC	No effect	No effect	No effect

Conclusion

Solventless paint indeed represents an attractive alternative to organic solvent based paint. In this work there was good compatibility between the copolymer binder synthesized with other paint ingredients, as the paint has shown no sign of phase separation even after 12 months. This paint confirmed good chemical resistance (in acidic, alkaline and salt medium).

Analytical data of the paints revealed superiority of HNSO/PVAC paint over PVAC paint. Also poor water resistance, hardness and brittleness associative with a typical PVAC was properly address as paint developed from HNSO/PVAC composite gave better viscosity, flexibility with no crack, adhesion and even opacity and was in agreement with SON. The use of HNSO/PVAC composite is recommended for use as a binder for Emulsion paint formulation.

References

1. AOAC, 2000. Official Methods of Analysis International (Horwitz W. Edition) Gaiithershur. USA. 17th Edition, 1(41): 30-35.

2. Ayoub, S., Taghi, T., Abolghasem, K. and Ahmadreza, S. 2013. Improving some of applied properties of oriented strand board (OSB) made from under-utilized low quality paulownia (*Paulownia fortunie*) wood employing nano SiO2. Indus. Crop. Prod., 42: 1-9.

3. Dimas, B.J., Osemeahon, S.A., Maitera, O.N. and Hotton, A.J. 2013. Influence of Starch Addition on Properties of Urea Formaldehyde/Starch Copolymer Blends for Application as a Binder in the Coating Industry. J. Environ.Chem. Ecotoxicol., 5(7): 181-189.

4. Emel Yildiz, Tulay Yilmaz, Huseyin Yildirim, Abdulkadir Kuyulu and Atilla Gungor. 2007. Thermal and Mechanical Properties of Poly (arylene ether ketone)s having Pendant Tertiary Butyl Groups. J. Polym. Res., 14: 61-66.

5. Ezeagba, J.U., Ikezu, U.J. and Lloh, E.O. 2014. Formation of an Oil Paint Using Alkyd Resin from Soya bean Oil. World Appl. Sci. J., 32(1): 83-87.

6. Habib, F. and Bajpai, M. 2011. Synthesis and Characterization of Acrylated Epoxidized Soybean Oil for UV Cured Coatings. Ch. ChT., 5(3): 317–326.

7. Huntsman, C. 2013. Titanium and Titanium dioxide Industry review. Retrieved August 22, 2013, from http://www.rsc.org/images/PDF1_tcm18-40441.pdf.

8. Hussain, A.I. and Nasr, H.E. 2010. The role of carboxylic acid on the characterization and evaluation seed emulsion of styrene/butyl acrylate copolymers lattices as paint. Nature Sci., 8(8):94-103.

9. Karakas, F., Pyrgiotakis, G., Celik, M.S. and Moudgil, B.M. 2011. Na-Bentonite and MgO Mixture as Thickening Agent for Water-Based Paints. KONA Powder and Particle J. No 29: 96-106.

10. Nigerian Industrial Standard (NIS) Test Methods for Paints and Varnishes, NIS 278. 1990. Standards Organization of Nigeria (SON), Lagos, Nigeria, part 6, pp: 1-28.

11. Nigerian Industrial Standard (NIS), Specifications for Emulsion Paints for Decorative Purposes, NIS:269. 2008 Standards Organization of Nigeria (SON), Lagos, Nigeria, pp: 5-13.

12. Oladipo, O., Ighodalo, C. and Olujinmi M.F., 2013, Formation and characterization of paint based on alkyd resin derivative of Xinenia Americana (wild olive) seed oil. Environ. Nat. Res. Res., (3): 53-55.

13. Osemeahon S.A. and Dimas B.J. 2014. Development of urea formaldehyde and polystyrene waste as copolymer binder for emulsion paint formulation. J. Toxic. Environ. Heal. Sci., 6(3): 75-88.

14. Osemeahon, S.A. 2011. Copolymerization of Methylol Urea with Ethylol Urea Resinfor Emulsion Paint Formulation. Afri. J. Pure Appl. Chem., 5(7): 204-211.

15. Osemeahon, S.A. and Archibong, C.A. 2011.Development of Urea Formaldehyde and Poly ethylene waste as a Copolymer Binder for Emulsion Paint Formulation. J. Toxicol. Eniron. Health Sci., 3(4): 101-108.

16. Osemeahon, S.A. and Barminas, J.T. 2007. Development of amino resin for emulsion paint formulation: Reactive blending of methylol urea with soybean oil. Afr. J. Biotech., 6(6): 803-809.

17. Osemeahon, S.A., Barminas, J.T. and Jang, A.L. 2013. Development of Waste Polystyrene as a Binder for Emulsion Paint Formulation I: Effect of Polystyrene Concentration. Int. J. Eng. Sci., 2(8): 30-35.

18. Osemeahon, S.A., Nkafamiya, I.I., Millam, C., and Modibbo, U.U. 2010. Utilization of Amino Resin for Emulsion Paint Formulation: Effect of Urea Formaldehyde Viscosity on Urea-Formaldehyde and Soybean Oil Polymer Composite. Afri. J. Pure Appl. Chem., 4(1): 001-006.

19. Petrovic Z Lj., Raspopovi´c Z.M., Dujko, S. and Makabe, T. 2002. Appl. Surf. Sci., 192: 1

20. Saadati, S.M., Mosslemin, M.H. and Behmadi, H. 2013. Synthesis and Characterization of Novel Polyamide-ethers Based on Bis-imidazole Containing Bulky Aryl Pendant Groups. Polímeros., 23(4): 484–92.

21. Shangde S., Xiaoqiao K., Longlong C., Guolong Y., Yanlan B., Song, F and Xiadi X. 2011. Enzymatic epoxidation of Sapindusmukorossi seed oil by perstearic acid optimized using response surface methodology'. Indus. Crop. Prod., 3(3): 676-682.

22. Surajudeen, A. and Zebulu , D.M. 2015. Production of Emulsion House Paint Using Polyvinyl Acetate and Gum Arabic as Binder. Int. J. Mat. Sci. Appl., 4(5): 350-353.

23. Zorba, T., Papadopoulou, E., Hatjiissaak, A., Paraskevopoulos, K.M. and Chrissafis, K. 2008. Urea-formaldehyde resins characterized by thermal analysis and FTIR method. J. Ther. Anal. Calorim, 92: 29-33.