Characterization of Emulsion Paints Formulated using Reactive – Dyed Starch as a Pigment

Abbas Kazaure Adamu, Muhammed Kabir Yakubu, and Olufemi Kassim Sunmonu

Abstract—Emulsion Paints were formulated using Reactive-Dyed Potato and Cassava Starch as Pigments at different pigment mass concentration (PMC) as 40%, 30%, 20%, and 10% respectively, and polyvinyl alcohol (PVA) as binder, with a dispersant and a solvent (Water).The effect of varying concentrations of pigments were studied and the higher (40%) concentration of pigment produced better result, as more compatibility with the binder, and deeper colour for the paints formulated were obtained. The formulated paints were characterized for physico-chemical properties such as viscosity, density, drying time, weathering, Light fastness, and IR Spectra which yielded positive results, and revealed that the paints could be used as both indoor and outdoor coatings.

Keywords— Binder, Paint, Pigment, Starch.

I. Introduction

PAINT is a term used to describe a number of substances that consists of a pigment suspended in a liquid or paste vehicle such as oil or water. However, paint is often referred to as material that may be applied as a continuous layer to a surface. Paint was traditionally used to describe pigmentary materials as distinct from clear films which are more properly called lacquer or vanishes. With a brush, a roller or a spray gun, paint is applied in a thin coat to various surfaces such as wood, metal or stone.

Paint has been recognized to provide aesthetic and protective requirements. Although it's primary purpose is to protect the surface to which it is applied, paint also provides decoration.

Paint making has been in existence since pre-historic era about 25,000 years ago among primitive men (Hunters and Dwellers) and probably inspired by the rock formation of their cave walls to outline and colour the shapes of the animals they hunted, survived in caves in France and Spain. Early artist relied on easily available natural substances to make paint such as natural earth pigments, charcoal, berry juice, land, blood and milk weed sap.

Later, the ancient Chinese, Egyptians, Hebrews, Greeks and Romans used more sophisticated materials to produce paints for limited decoration, such as painting walls. Oils were used as varnishes and pigments such as yellow and red ochres, chalk, arsenic sulphide yellow, and malachite green were mixed with binders such as gum Arabic, lime egg albumen and beeswax.

Paint was first used as a protective coating by the Egyptians and Hebrews, who applied pitches and balsams to the exposed wood of their ships.

During the middle ages artists began to boil resins with oil to obtain highly miscible (mixable) paints, and artists of the fifteenth century were the first to add drying oils to paint, thereby hastening evaporation.

In Boston around 1700, Thomas child built the earliest American paint mill, a granite through within which a 1.b foot (0.5 meter) granite ball rolled, grinding the pigment. The first paint patent was issued for a product that improved white wash, a water slaked lime often used during the early days of United States. In 1865, D.P film obtained a patent for a water-based paint that also contained zinc oxide, potassium hydroxide, resin, milk and linseed oil. Today, synthetic pigments and stabilizers are commonly used to produce uniform batches of paints.

New synthetic vehicles developed from polymers such as polyurethane and styrene butadiene emerged during the 1940s. Alkyd resins were synthesized, and they have dominated production since.

The first step in making paint involves mixing the pigment with resin, solvents and additives to form a paste. If the paint is to be for industrial use, it is usually routed into a sound mill, a large cylinder that agitates tiny particles, making them smaller and dispersing them throughout the mixture.

A paint is composed of pigments, solvents, resins and various additives. The pigments give the paint its colour, solvents make it easier to apply, resins help it dry, and additives serves as everything from fillers and so on. Today, paints are used for interior and exterior house paintings, boats, automobiles, planes, appliances, furniture, and many other places where protection and appeal are desired (9).

The purpose of paints and surface coatings is two-fold. They may be required to provide the solution to aesthetic or protective problems or both.

For example in painting the motor car the paint will be expected to enhance the appearance of the car body in terms of colour and gloss, and if the body is fabricated out of mill steel it will be required to give protection against corrosion. If the body is formed from glass fibre reinforced plastic the paint will only be required for aesthetic purposes (3).

Composition of Paints

The components of paint are: vehicles, pigment, extenders,

Abbas Kazaure Adamu is with Hussaini Adamu Fedral Polytechnic, Kazaure Nigeria. Phone Number: +234 703 1259 933,

binders and additives. However, not all paints have every ingredients represented e.g. gloss paints will not contain extenders (3), which are organic coarse particle materials.

The paint can be air or stove dried (heated). Vehicle in paint, is the medium in which the pigment and other additives are carried on in the surface coating. The vehicle functions to provide means for easy application; provides means of adhesion to the surface, facilitates, drying of the paint and acts as a moisture barrier.

The pigments are insoluble particles, which cover the surface in which the paint is applied. The pigments are the source of colour for paints and can be organic or inorganic. They are required to resist dissolution in solvents which they may contact so as to minimise problems such as “bleeding” and “migration”. In addition to solvent resistance, pigments are required to be fast to light, weathering heat and chemicals such as acids and alkalis. However, for most applications, the optical properties of pigments are of prime importance.

Extenders and fillers are incorporated in paints to provide opacity and for a variety of purposes.

Binders used are the resins which bind the pigment. They are homogenously dispersed in the dry film former

II. Experimental Procedure Paint Formulation

The following reagents were used during the paint formulation

a. Pigment (Blue and Yellow)
b. Binder (polyvinyl alcohol (PVA)
c. Dispersant
d. Solvent (water)

The paint was formulated using the pigment mass concentration (PMC), 10%, 20%, 30% and 40%

Thus:

The following Table represent the recipe used during the paint formulation in each case for both the Blue and Yellow emulsion paints.

TABLE I
RECIPE FOR THE PAINT FORMULATION

%pigment	Pigment mass	Binder	Solvent	Dispersant
10%	0.22g	10g	2mls	0.1g
20%	0.50g	10g	2mls	0.1g
30%	0.86g	10g	2mls	0.1g
40%	1.33g	10g	2mls	0.1g

Procedure

The polyvinyl alcohol (PVA) binder and pigment were mixed thoroughly in a small bottle container using glass rod, the dispersant was dissolved in the solvent (deionised water) and added to the pigment binder mixture and agitated continuously for one hour (1hr) each to ensure homogeneity to the mixtures.

The same procedure was used for both the Blue and Yellow paints formulations using different concentrations of pigment.

Characterization of the formulated paints

The following tests were carried out to determine the physico-chemical properties of the formulated paints.

Viscosity

A solution containing 1ml of each of the paint samples from 10%, 20%, 30% and 40% paints formulated in 100mls of deionised water (solvent) were prepared and used during the viscosity measurement. The flow time of the solvent (water) was first determined and represented as to and the flow time for that of the prepared paint solution which is represented as t was also determined. These flow times were all determined at ambient temperature which was around 28^0C.

Equation I

$$l_2 = \frac{l_1 t_o \ell_2}{t \quad \ell_1} \qquad or \qquad l_2 = \frac{l_1 t_2 \ell_2}{t_1 \ell_1}$$

Where t_1 = flow time of water
ℓ_1 = Density of water
ℓ_2 = Density of Paint solution
l_2 =Viscosity of paint solution
t_2 = Flow time of paint solution
l_2 = Viscosity of water

Density Determination

The density of each of the paint solutions was determined gravimetrically using density bottle.

The mass of the bottle was first determined as well as that of mass of the density bottle filled with the paint solution and when filled with water.

Thus;
Mass of density bottle alone = w_0
Mass of density bottle with water = w_1
Mass of density bottle with paint solution = w_2

Equation II

$$\text{Density of paint} = \frac{w_2 - w_o}{w_1 - w_o} glcm^3$$

Drying Time

The drying time of each of the formulated sample and of commercial paint was determined. The paint samples were applied on white cardboard substrate and their respective drying times determined by exposure to air and recorded.

Fastness to Light

The light fastness properties of the paint were evaluated using standard procedures as it is done to evaluate the light fastness properties of the dyed fabrics as described by (6). The test was carried out using MK1 artificial light fastness tester which is fitted with mercury-tungsten (MBTF) 500 watts lamp.

The samples of paint coated patterns were mounted side-by-side with the blue wool standard on the tester and the tester was switched on, thus exposing the paint samples and the standards for 96 hrs. The exposed and unexposed paint patterns as well as the blue wool standards were then compared to evaluate the degree of resistance of the paint to light.

Weathering Test

Weather ability (i.e. outdoor durability) of emulsion paint coating like other coating systems is expressed as change in gloss, chalking, color retention, cracking, embrittlement, and weight loss (8). All these processes are influenced by nature, like solar radiation, temperature, moisture, chemical pollutants, oxygen, and biogranisms.

The samples of the formulated paint patterns along side with the commercial paint sample patterns were exposed in an open air during the weathering test for 604hrs. Both samples were then compared to evaluate the degree of degradation of the different types of paints.

Infrared (IR) spectroscopy

IR is the spectroscopy that deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques mostly based on absorption spectroscopy, the infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration, either stretching or bending. Different types of bonds and thus different functional groups, absorbs infrared radiation of different wavelength. An IR spectrum is a plot of wave number (X-axis) Vs percentage transmittance (Y-axis).

The IR spectras of the dyes-starches (pigments) and that of the formulated paints were obtained by running the samples in an IR spectrometer, some of the wavelength are absorbed while some are Transmitted. Identification of bonding can also be made by considering the use of the differences in the finger print regions.

III. Results and Discussion

A. Paint Formulation

The yellow and blue emulsion paints were formulated using the reactive dyed starch as pigment. During the formulation, polyvinyl alcohol (PVA) was used as the binder, which gave good compatibility with the pigment in each case. The paints were formulated using different pigment mass concentration (PMC) as 40%, 30%, 20% and 10% respectively. The 40% PMC showed more levelness and gave a deeper coloured paints in all the cases. However, the higher the PMC used the more the compatibility and the deeper the colour obtained for both the yellow and blue paints produced. The paints showed good flow property which made them easy to apply and was also found to possess high opacity.

B. Characterization of the Physco-Chemical Properties of the Formulated Paints

Viscosity

The viscosities of the formulated paints were obtained using the Ostwald viscometer at an ambient temperature of about 26°C and were represented in the table below.

However, the paints showed moderate viscosity which indicated good flow property

TABLE II
VISCOSITIES OF THE PAINT SAMPLES AT DIFFERENT PMC

	%PMC Viscosities (Poise)			
Paint sample	40%	30%	20%	10 %
Reactive-dyed potato starch pigment (paint)	0.915	0.879	0.8916	0.8656
Reactive Tectilon Blue 4G-Dyed Potato Starch Pigment (paint)	0.9281	0.8956	0.8838	0.8714
Reactive Tectilon Yellow 2G Dyed Cassava Starch Pigment (Paint)	0.9192	0.9048	0.8946	0.8876
Reactive Tectilon Blue 4G-Dyed Cassava Starch Pigment (Paint)	0.8981	0.8923	0.8678	0.8609
Commercial Paint	0.94337 Poise			

From the results of the viscosity measurement, it indicated that PMC had some influence on the viscosity. The 40% PMC had the highest viscosity in all the cases. The higher the pigment mass concentration (PMC) the higher the viscosity of the paint obtained, the commercial paint showed a higher viscosity than all the formulated paints.

The low viscosity paint produced showed good levelling, with high opacity. The gloss of the paints was also higher. The paints were associated with having low spattering when coated on cardboard substrate. The low viscosity of the paints formulated accounts for high tendency of its movement and easy application.

They also smooth out faster.

This result had revealed that the paint performance is influenced by the molecular weight or viscosity as similarly revealed by (1) who maintained that if low and high viscosity grade cellulose either products are compared, the comparison s usually done at the same paint viscosity (at a defined shear rate). This means paint will contain more of a low viscosity (low. Mol. wt) cellulose either as compared to a high viscosity (higher mol. wt) cellulose either to obtain the same paint viscosity.

If you work with oil or acrylic paint, you have probably tried to tweak the properties of the paint by thinning it out or by thickening it up. Both of these actions affect the viscousity of the paint, along with a number of other properties. The thicker more viscous paint resist gravity better and doesn't slide down the canvas-it stays put. The individual small areas within a splotch of the thicker more viscous paint are also better at staying put (IV).

TABLE III
RESULTS OF THE DENSITIES OF THE PAINT SAMPLE

Density of paint sample	%PMC			
	40%	30%	20%	10%
Reactive-Tectilon Yellow 2G- dyed potato starch pigment (paint)	1.0032	1.0028	0.998	0.997
Reactive Tectilon Blue 4G-dyed potato starch pigment (paint)	1.0033	1.0029	1.0021	1.0019
Reactive Tectilon Yellow 2G-dyed Cassava starch-pigment (paint)	1.0040	1.0039	1.0028	1.0025
Reactive Tectilon Blue 4G Dyed cassava starch pigment (Paint)	1.0036	1.0024	0.9830	0.9813
Commercial paint	1.01326			

Density

The densities obtained by the formulated paints as shown in the table below indicates that cassava pigment showed the highest densities of 1.0040, 1.0039, 1.0028 and 1.0025 for 40%, 30%, 20% and 10% PMC respectively.

The densities of the paint changed with the pigment mass concentration(PMC); such that the higher the PMC, the more the densities of the paint in each case. However, this may be due to the influence of the pigment, additive and other paint ingredients.

The commercial paint showed a higher density 1.0136, a small increase compared to all the formulated paints.

TABLE IV
RESULT OF THE DRYING TEST OF THE PAINT SAMPLE

	%PMC			
	40%	30%	20%	10%
Reactive Tectilon Yellow 2G- Dyed potato starch-pigment (paint)	5-10min	5-10mn	5-10min	5-10min
Reactive Tectilon Yellow 2G- Dyed cassava starch-pigment (paint)	5-10min	5-10min	5-10min	5-10min
Reactive Tectilon Blue 4G-Dyed Potato starch pigment (paint)	5-10min	5-10min	5-1min	5-10min
Reactive Tectilon Blue 4G-Dyed Cassava Starch-pigment (paint)	5-10min	5-10min	5-10min	5-10min
Commercial Paint	20-30min			

Drying Time

The results of the drying time test obtained showed that all the formulated paints dried between 5-10 min, much faster than the commercial paints which dried between 20-30min. This revealed a good property of the formulated paints.

Light Fastness

TABLE V
RESULTS OF THE LIGHT FASTNESS TEST OF THE PAINT SAMPLES

	%PMC			
Paint samples	40%	30%	20%	10%
Potato starch pigment-yellow (paint)	6 -7	6-7	6-7	6-7
Potato starch pigment-blue (paint)	6 -7	6 -7	6 -7	6 -7
Cassava starch pigment-yellow (paint)	6 -7	6 -7	6 -7	6 -7
Cassava starch pigment-blue(paint)	6 -7	6 -7	6 -7	6 -7

The result of the light fastness test revealed that both the paint coated substrate patterns (cardboard) possess very good to excellent light fastness properties. After the 96hr light fastness test, the exposed samples along side with the blue wool standards where compared with unexposed samples which showed that both the exposed and the unexposed yellow and blue paint patterns could not be distinguished.

All the yellow and blue paint coated patterns were rated 6-7 which showed that the paints produced can be reliable for use as both indoor and outdoor coatings.

According to these results, pigment mass concentration (PMC) has not much effect on the light fastness properties because all the paint samples were within the same fatness range. The only difference is deepness of the shade which is due to the difference in percentage P.M.C

Weathering Test

After the exposure of the paint coated patterns (cardboard) for about 604hrs outdoors, the result showed that both the formulated paints coated patterns and the commercial paint coated patterns when compared possessed high degree of resistance to weathering. Both the samples cracked to a little extent when bent and no change of colour and appearance was observed on the surface of the test patterns.

The first sign of a change in the coated film during weathering is matting of the surface (8). The stages in loss of a high coating gloss during weathering were found as follows.

1. The initial smooth and glossy surface losses the last residues of solvent in the first few weeks or months. The surface shows the first signs of shrinkage render the largest pigment agglomerates slightly visible at the surface of the film.
2. Degradation of the film then begins, the more stable pigments became concentrated and gloss is lost, the film becoming more matted and flat, Monitoring of gloss retention and surface during weathering has been employed to assess the durability of coatings.

Result of the Infrared (IR) Spectroscopy

IR spectra of the Dyes, starches and dyed starches are presented. The appearance of strong bands 3742.92cm^{-1}, 3741.33cm^{-1}, 3740.73cm^{-1}, 3738.47cm^{-1}, 3734.38cm^{-1}, 3732.78cm^{-1} and 3740.07cm^{-1} is attributed to (N=N) and the appearance of strong bands and broad bands in the region 3373.64cm^{-1} and 3352.89cm^{-1} indicated the presence of (OH) group on the starch spectra.

The appearance of strong bands 2924.54cm^{-1}, 2925.18cm^{-1}, 2924.64cm^{-1}, 2924.56cm^{-1}, 2924.7cm^{-1} and 2924.01cm^{-1}, indicated the presence of Ar-H. The appearance of strong bands 2364.27cm^{-1}, 2362cm^{-1}, 2361.53cm^{-1}, 2360.99cm^{-1} 2360.45cm^{-1}, 2359.67cm^{-1} and 2359.41cm^{-1} indicated the presence of C=N. Also the appearance of strong bands 16.49.63cm^{-1}, 1696.51cm^{-1}, 1694.54cm^{-1} is attributed to the presence of carbonyl group.

The disappearance of OH peak at 3373.64cm^{-1} and 3353.89cm^{-1} on the dyed Cassava and Potato starch spectras respectively is an indication that there is a covalent interaction between the starch and the dye molecule, as according to (VII). The differences in the finger prints regions of the dyes, starches and dyed starches spectras, 1024.60cm^{-1}, 669.06cm^{-1}, 1026.05cm^{-1}, 669.60cm^{-1}, 1034.33cm^{-1}, 908.86cm^{-1}, 1031.99cm^{-1}, 908.92cm^{-1}, 890.67cm^{-1}, 672.47cm^{-1}, 889.42cm^{-1}, 509.53cm^{-1}, 1031.24cm^{-1}, 911.78cm^{-1} and 1022.21cm^{-1}, 902.47cm^{-1} respectively indicated that there was an interaction between the dyes and starches molecules. These peaks appeared in similar manner all through

IV. CONCLUSION

The work has shown that there was a good compatibility between the pigment and the binder during the paint formulation, which accounts for the deeper colour and good opacity for paints formulated. Characterization of the physico-chemical properties of the paints indicated good properties associated with the paints such as, good opacity, weathering resistance, excellent light fatness and quick drying. The paints were also found to have moderate viscosity which accounts for good flow properties.

These results have revealed that the paints formulated could be used as both indoor and outdoor coatings. And if further characterizations could be carried out such as NMR spectroscopy, impact test, cross hatch test, pencil hardness test and many more, the surface appearance of the paint coating and many other properties could be improved.

REFERENCES

[1] Don, W. (2011) The Influence of Viscosity of the Cellulose Either on Paint Performance http://www.bing.com/searchq=dontwolf%23

[2] Isyaku S. (2003), Study of Physico-Chemical Properties of Alkyd Resin Derived from Some natural Glycerides. Unpublished M.Sc. Thesis, Bayero University, Kano pp 69-70.

[3] Lambourne, R. (1987) Paint Composition and Applications, A General Introduction. Introductory Paint Technology Ellis Horwood Publishing Limited pp25-29 and Pp122-126

[4] Mc Cann, (1984) Paint and Coating Manufacture, U.S National Institution for Occupational Safety and Health (NIOSH), Wikipedia the free encyclopaedia http://www.scribd.com/doc/47766018.

[5] Nerdly, P. (2011) Viscosity, Why Does it Matter A blog on Art and Science, the Science Behind Art Materials and the Art of Science. http://www.nerflypaiter.com

[6] Nkeonye, P. O. (1987), Textile fibres and dyes, Fundamental Principles of Textile dyeing, Printing and finishing, Ahmadu Bello University, Press, Zaria, Nigeria Pp 1-23.

[7] Rotimi, O. (2001), Efficacy of Dibutyltin DIcarboxylates as Alkyd Paint Stabilizers. Unpublished PhD Thesis, Ahmadu Bello University, Zaria Nigeria Pp. 7, 48 193.

[8] Philip et al. (1988), Organic Structure analysis, Oxford University Press, New York

[9] Wikipedia, the Free Encyclopaedia, Emulsion and Water Soluble Paints and Coatings. http://en.wikipedia.org.wikiemulsionpolymerization Dec.15,2011at 22:19.