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PAINTS FORMULATION USING DIISOCYANATES AND 1,4 –DIAMINO ANTHRAQUINONE (1,4 DAQ) AS PIGMENTS AND POLYVINYL ALCOHOL AS BINDER, CHARACTERIZATION AND THEIR APPLICATION ON WOOD SUBSTRATE

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ABSTRACT

The Paint and coatings industry produces a huge variety of products that protect, preserve, and also beautify the objects to which they are applied, however, the components are expensive, therefore there is the need to look for alternative constituents which are cheaper and more durable. Emulsion Paints were formulated using colourants produced from diisocyanates and 1,4 diamino anthraquinone and polyvinyl alcohol as binder. The constituents of the paint was stirred mechanically in a ceramic mortar and pestle for 1 hour, and it was applied on the substrate (ceiling board). The coated samples were subjected to physical characterization, viscosity, surface drying time, weathering and lightfastness and compared with a commercial paint (Emulsion paint). The results indicates a very good light fastness property of 6-7, for paints produced from hexamethylene diisocyanate and where resistant to weathering, while paints produced from 1,4 phenylene diisocyanate showed a poor light fastness of 1-2, however it also indicated resistant to weathering. Hexamethylene diisocyanate, is less expensive and is more durable and economical in emulsion paint production compared to 1,4 phenylene diisocyanate which fades easily and is also expensive.

Keywords: Polymerization, Copolymerization, Formulation, Characterization, Paint, Diisocyanates, 1,4-diamino anthraquinone

INTRODUCTION

Natural and synthetic dyes are compounds of great interest since they play an important role in our everyday life. The broad variety of technical and industrial applications, which includes ―classical‖ utilizations like dyeing of textiles and other consumer goods as well as rather new usages such as laser dyes and dyes for organic light emitting diodes (OLEDs), liquid crystals (LC) displays, optical data storage and fluorescent labeling, has produced a great deal of research in this field. The main driving force is the constant demand for improved dyeing efficiency (Abou-Okeil et al, 2010; Morris et al, 2008) or photochemical/photophysical properties (Baptista and Indig 1998; Mula et al, 2008) while also focusing on eco-friendly procedures (Mirjalili et al, 2011; Sulak and Yatmaz, 2012) reduced toxicity (Abadulla et al, 2000; Lee and Pavlostathis,2004) and decreased production costs (Warner et al, 2004).

A promising approach to fulfilling these requirements is the combination of dyes and polymeric materials, the great advantage of such systems is the controllability of many features like solubility, stability, and toxicity through appropriate choice of polymeric material. The binding modes leading to the formation of dye-polymer conjugates can be either covalent or non-covalent. While the first approach requires the formation of covalent bonds, non-covalent binding can occur through different kinds of interactions such as ionic and dipole dipole interactions or through the formation of inclusion complexes. An example of non-covalent attachment is sugar-based polymers. Due to the large number of polar substituents that enable the formation of dipolar interactions with adequate substrates, sugar-based macromolecules are suitable materials for the supramolecular attachment of dyes. Such oligo/polysaccharides can be obtained from natural products (e.g, starch, cellulose, chitosane) or chemical linkage of monomeric subunits and are therefore readily accessible. The efficient adsorption of anionic azo dyes bearing sulfonate moieties to starch and β-cyclodextrin polymers was reported (Ozmen et al, 2008; Yilmaz et al, 2007). In the underlying studies, the polymers were prepared by cross-linking of β-cyclodextrin and starch, respectively with hexamethylene diisocyanate. A large number of synthetic routes can be found in the literature that allows for the covalent emplacement of dye molecules in polymeric materials. These can generally be categorized under the following approaches. (1) Polymerization of coloured monomers. (2) Polycondensation or (cross) coupling reactions of adequate dyes/dyes derivatives. (3) Polymer-analogous attachment of dye molecules to preformed polymers. (4). Preparation of high molecular weight derivatives of single chromophores (e.g. via grafting onto mechanism). The preparation of polymeric dyes for technical and industrial applications is mainly conducted via routes 1-3, since the corresponding materials contain a higher tinctorial strength than the high molecular weight derivatives of single chromophores (Dawson, 1981).

Polymerization of coloured monomers by conversion of dye molecules into polymerizable derivatives followed by their copolymerization is a valuable approach for the preparation of dye-containing polymers. Several examples of azo dyes being converted into radically polymerizable compounds are known. An interesting example is acrylate azo dyes for materials applied in non-linear optics (Robello, 1990).

MATERIAL AND METHODS.

Materials

Polyvinyl alcohol (PVA), ammonia, kerosene, formaldehyde, kaolin, Titanium dioxide (TiO_2), Calcium carbonate ($CaCO_3$), Ceramic mortar and pestle, mechanical stirrer, distilled water, Ubbelohde viscometer, was available in the Department of Polymer and Textile Engineering, Ahmadu Bello University Zaria, Nigeria, pigment or colourant F to J (Pigment from hexamethylene diisocyanate and 1,4 DAQ) and P to T (Pigment from 1,4 phenylene diisocyanate and 1,4 DAQ).

Methods

Production of Paint based on polyvinyl alcohol (PVA). Preparation of (PVA) Stock.

PVA, 50g was dissolved in 600ml of distilled water, it was covered and allowed to stay overnight at room temperature (25°C). It was then stirred with a mechanical stirrer for 5 hours until a homogenous solution was obtained. The stock was poured into an airtight container to avoid skinning.

Table 1: Paint Formulation - The recipes used

Recipe	Mass (g)
PVA	10
Ammonia	0.04
Kerosene	2
Formaldehyde	0.2
Kaolin	0.2
TiO_2	0.2
$CaCO_3$	0.4
Pigment	0.39
Total	13.43

Grinding of the pigment F to J, P to T and mixing of paint was achieved using a ceramic pestle. The mixture was stirred continuously, followed by the addition of 10ml of distilled water. Stirring continued for one (1) hour. PVA was selected as a binder because it is soluble in water and most importantly, it is biodegradable. Titanium dioxide was incorporated to serve as an extender as well a light sensitizer. The resulting paint was poured into a clean and air tight container for further characterization. The same procedure was adopted using the remaining nine pigments and utilizing a 3% pigment mass concentration (PMC).

Application Of Paints to Substrate

The paint was applied on a particular wood popularly known as Duratex, a brazil ceiling board acquired from samara market, Zaria, Nigeria. The samples of 20mm×50mm were cut cleaned and dried. One inch (1’’) chuto bristle handbrush was used for the application of paint. Ten (10) coated samples were produced from the corresponding nine (9) paints formulated plus one (1) commercial paint (control).

Physico-Chemical Characterization of paints

Ranges of tests were conducted on the formulated coatings such as surface drying time, weathering, viscosity and light fastness.

Surface drying time.

This measure the relative degree of cure (dry to touch). It was measured by the quantitative finger marking test (Ali et al, 2001). The sample was painted using a handbrush, and the time taken for a coated sample to dry was measured by sporadically touching the coatings with small white paper until there was no stain noticed on the paper. The timing was achieved using a stopwatch. The experiment was repeated for the produced paints including the commercial paint which serve as control. The results are shown in Table 2.

Weathering

The samples were exposed outside for three hundred and eighty-four (384) hours to test the resistance of the samples to harsh weather conditions.

Viscosity measurement

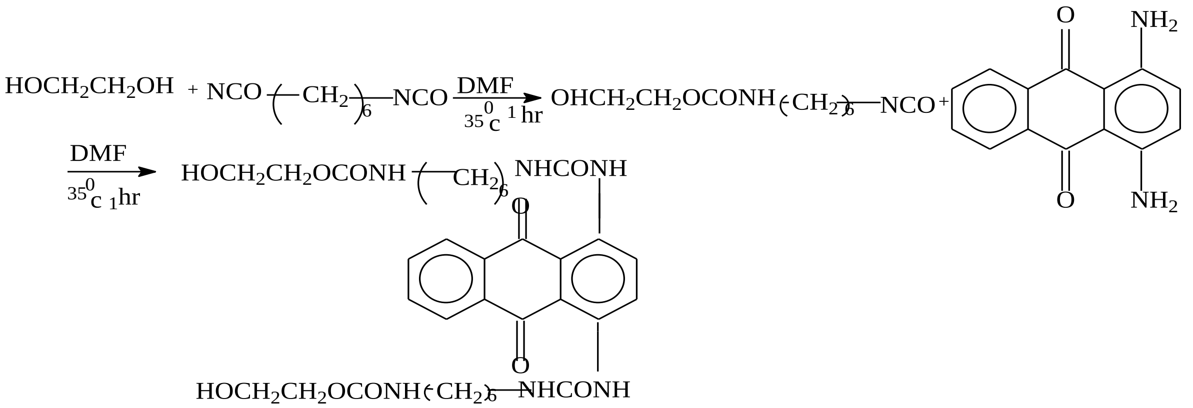
This was measured using Ostwald viscometer. The viscometer was thoroughly rinsed with distilled water and drained. The temperature of the viscometer was maintained at 30°C and securely fastened with the upright tubes exactly vertically. The data obtained was by taking 10ml each of the paint, with a stringe, and placing it in a viscometer. The time for running the paint through the Ostwald viscometer in seconds is multiplied by the viscometer value (1724) and the results are shown in Table 4.

Light Fastness Test

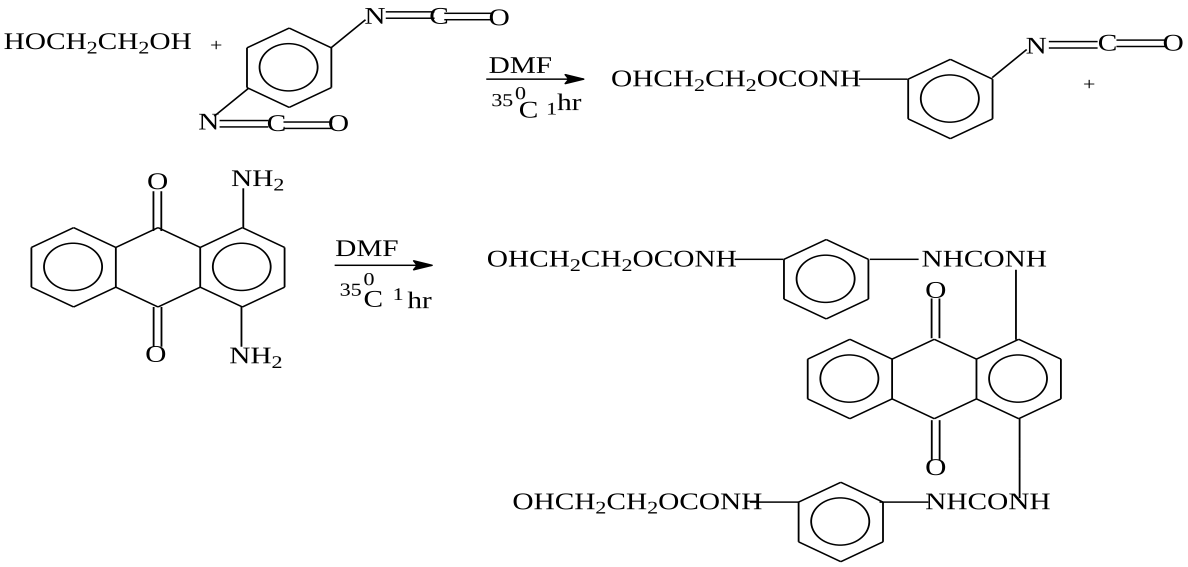
The light fastness of the formulated and control paints, on the coated substrate was determined according to a standard procedure.

RESULT AND DISCUSSION

Synthesis of the polymeric colourants (Pigment).



Scheme 1. Reaction of ethylene glycol with hexamethylene diisocyanate crosslinked with diamino anthraquinone (1,4).



Scheme 2. Reaction of ethylene glycol with 1,4-phenylene diisocyanate crosslinked with diamino anthraquinone (1,4)

Surface Drying Time

This measures the relative degree of cure (dry to touch). It was measured by the quantitative finger marking test (Ali et al, 2001). The paint surface drying time is less compared to that of the emulsion standard drying time, which is an indication of an improvement in the drying time of the standard paint. This is shown in Table 2.

Table 2: Paint surface drying time

Pigments of paint	Time (secs)
F (1,4 DAQ)	362
G (1,4 DAQ)	373
H (1,4 DAQ)	379
I (1,4 DAQ)	383
J (1,4 DAQ)	393
P (1,4 DAQ)	424
Q (1,4 DAQ)	440
R (1,4 DAQ)	435
S (1,4 DAQ)	433
T (1,4 DAQ)	468
Emulsion standard	600

Weathering

The samples were exposed outside for three hundred and eighty four (384) hours. Observation was made on the impact of environmental conditions which the samples were subjected to, the coated paint did not exhibit sign of cracking or peeling. This shows that the paint can be effectively used for outdoor purposes as shown in Table 3 below.

Table 3: Weathering Test Result

Paints	Cracking	Peeling
F (1,4 DAQ)	OK	OK
G (1,4 DAQ)	OK	OK
H (1,4 DAQ)	OK	OK
I (1,4 DAQ)	OK	OK
J (1,4 DAQ)	OK	OK
P (1,4 DAQ)	OK	OK
Q (1,4 DAQ)	OK	OK
R(1,4 DAQ)	OK	OK
S (1,4 DAQ)	OK	OK
T (1,4 DAQ)	OK	OK

Viscosity Measurement

The viscosity of the paints was found to increase from F to J (1,4 DAQ) and P to T (1,4 DAQ) because of the variation in the molar mass of the repeat units and the molar mass of the polymeric colourant used(Gumel et al, 2012; Robert and Robert 2001) as shown in Table 4 below.

Table 4: Viscosity Measurement of Paints

Paint	Poise
F	3122164
G	3134232
H	3146300
I	3166988
J	3196296
P	3139404
Q	3173884
R	3185952
S	3196296
T	3204916
Distilled water	167228
Standard (Acrylic emulsion)	3246292

Light fastness Test

The results obtained for the light fastness test for paints F to J (1,4 DAQ) gave a very good light fastness test (6-7) compared to paints P to T (1,4 DAQ) which shows a poor light fastness of (1-2), this can be attributed to the benzene ring attached to the diisocyanate group which reduced its tendency for intermolecular forces of attraction, secondly paints F to J (1,4 DAQ) is said to be more linear compared to paints P to T (1,4 DAQ), the linearity in the chain gives rise to a very good light fastness properties (6-7) (Robert, 2000). This is as shown in Table 5

Table 5: Light Fastness Test of Paints

F (1,4 DAQ)	6
G (1,4 DAQ)	6
H (1,4 DAQ)	6
I (1,4 DAQ)	7
J (1,4 DAQ)	7
P (1,4 DAQ)	1-2
Q (1,4 DAQ)	1-2
R (1,4 DAQ)	1-2
S (1,4 DAQ)	1-2
T (1,4 DAQ)	1-2

CONCLUSION

Emulsion paints were formulated using colourants produced from diisocyanates and 1,4 diamino anthraquinone, and polyvinyl alcohol as a binder and it was applied on the substrate (ceiling board), the result of the surface drying time of the paint produced is less compared to that of the emulsion standard drying time. Weathering test also indicated that the paint did not exhibit signs of cracking or peeling. Similarly, results of the light fastness test show that paints produced from hexamethylene diisocyanate gave very good light fastness (6-7), compared to paints produced with 1,4 phenylene diisocyanate which gave poor light fastness (1-2). Hexamethylene diisocyanate, is less expensive and is more durable and economical in emulsion paint production compared to 1,4 phenylene diisocyanate which fades easily and is also expensive.

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