

# Preparation of Starch-Reactive Dyed Pigment to Be Used In Emulsion Paint Formulation

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## Abstract

Starch samples were extracted from sweet potato and cassava using wet extraction method. The samples were then dyed with Reactive Tectilon Yellow 2G and Reactive Tectilon Blue 4G. The absorbance of the dyes were taken before and after dyeing and absorption isotherm plotted so as to determine the optimum concentration of dye to be used. The dyed starches were then washed, filtered, dried and finally grounded to fine particles to be used as pigments in paints.

**Key words:** Paints, Pigments, Reactive Dyes, Starch.

## I. INTRODUCTION

THE first description of starch and its application was known in the historical records of a much later period. This was given by Cato in a Roman treatise on agriculture written about 170BC. According to his method, a cereal grain was steeped in water for 10 days. The water was removed and the grain was pressed and stirred with fresh water.

The mixture was allowed to stand, and the precipitated material was pressed in a linen cloth, creamy liquid filtrate was collected in a clean vessel and then washed once more with fresh water. Finally, the material was allowed to dry in the sun.

The use of starchy products was dated to the late Neolithic-Chalcolithic but predynastic period of about 4000 BC – 35 BC as there was strip of Egyptian Papyrus, cemented together with a starchy adhesive. The use of starch products in sizing Papyrus by ancient Egyptians showed empirical development. Adhesive was made from fine wheat-flour, which was boiled with a dilute solution of vinegar. This paste was spread over a strip of Papyrus, the strip was beaten with a mallet and a second layer of paste and Papyrus was applied. It was stated that the sheets which were more than 200 years old, were still in good condition<sup>[6]</sup>.

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Although Pliny noted that starch was used for whitening cloth as well as for powdering the hair, but it did not seem to have been used for sizing textiles in early times.

In the early fourteenth century, starch introduced into Northern Europe to stiffen linen. Coloured and uncoloured starches were also used as cosmetics. Uncoloured starch was used principally as a hair powder; blue starch was employed by the puritians until its use was banned by the English Queen in 1596. Yellow starch was also quite fashionable until a notorious woman prisoner wearing bright-yellow starched ruffle was publically executed. Red starch for cosmetics remained in fashion for many years.

Wiesner (1965), reported that starch size was present in a Chinese document dated to 312 AD, and credited the Chinese to be the first to use size.

The American Potato starch industry is not nearly as old as European; potato starch was first produced in the United States in 1811 in New Hampshire.

In the early years; special varieties of potatoes were grown for starch manufacture much as is now done in Europe. These varieties were not of good cooking quality but contained a relatively large amount of starch<sup>[8]</sup>.

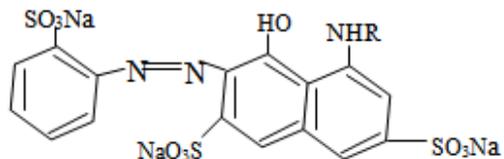
In Japan; sweet potato starch manufacture became an important industrial operation and constituted about two-third of the starch production of starch for 1964 was 80,000 tons from sweet potatoes; 200,000 tons from white potatoes, 250,000 tons from corn, and 50,000 tons from wheat.

The manioc plant, valuable for its large tuberous root are rich in starch; thrives in most equatorial regions between the tropic of cancer and the tropic of Capricorn. It is known by various names such as Yucca (Central America); Mandioca (South America) and cassava (Africa

and Southeast Asia). Most modern tapioca starch manufacturing plants use fresh cassava roots grown by proven agricultural methods[3].

Tapioca (cassava); for many years a prime product of the East Indies, is still produced there in large amounts, although production in the Dominican Republic and Brazil has assumed significance.

Reactive dyes were introduced in 1956 by the ICI limited and are presently the most versatile class of dyestuffs for the production of fast light shade cellulosic materials. It is also used in other applications. They derived their name from the fact that they react chemically with the fibre during dyeing; so that at the end of the dyeing process, both dye and fibre are linked together by strong covalent chemical bond to give dyeing of high fastness to wet treatments. This property is not possessed by any other class of dyes for cellulose. Reactive dyes, owed their reactivity to the presence in their structure of a reactive group which enables the dye to react with suitable groups in the fibre[4]. In most reactive dyes, the reactive group is linked to the chromophore via a bridging unit (e.g. –NH-group) but in some few others this group is attached directly to the chromophore.



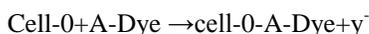
R, represents the reactive group, which varies from one range to another.

Reactive dyes are generally divided into two according to how they are applied to substrate. They are:

- (i) Nucleophilic substitution types and
- (ii) Nucleophilic addition types.

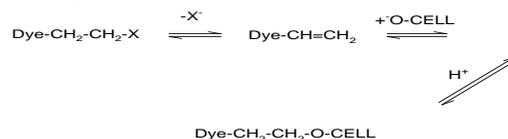
In the Nucleophilic substitution types reactive dyes, the dyes react with the cellulose by a Nucleophilic substitution mechanism, whereby a leaving group in the dye structure is displaced as a result of an attack by the cellulosate anions (cell-O)

e.g.



In the Nucleophilic addition type reactive dyes, the dyes are characterized by the fact that the dye-fibre reaction (or attachment) is that of addition, whereby a positively polarized

unsaturated carbon-carbon double bond in the dye reactive group is attached by a Nucleophilic group present in the fibre (cellulosate anion)



Pigments are materials which are solid particles largely insoluble in the film former, and in the solvents or diluents used in the paints and capable of being dispersed in the paints constituents to give maximum benefits in terms of the required properties of the paints. Pigments are the source of colour for paints and can be organic or inorganic. It is mixed with the binder to produce paint for protective and or decorative purpose. They contribute most of the principal functions as colour, opacity and anti – corrosion properties [5].

In addition to solvent resistance, pigments are required to be fast to light, weathering, heat and chemicals such as acids, and alkalis. For most applications, the optical properties of pigments are of prime importance.

Naturally occurring pigments such as ochre's and iron oxides have been used as colorants since prehistoric times. Archaeologists have uncovered evidence that early humans used paints for aesthetic purpose such as body decoration. Two examples include red ochre, anhydrous FeO<sub>3</sub> and the hydrated yellow ochre (FeO<sub>3</sub>H<sub>2</sub>O).

Before the industrial revolution, the range of colour available for art and decorative uses was technically limited. Most of the pigments in use were earth and mineral pigment from unusual source such as botanical materials, animal wastes, insects and mollusks were harvested and traded over long distances.

Biological pigments were often difficult to acquire and the details of their production were kept secret by the manufacturers. Tyrian purple is a pigment made from the mucus of one of several species of murex snail[9]. These pigments include; alizarin (synthesized) alizarin crimson (synthesized), cochineal red, rose madder, indigo, Indian yellow, Tyrian purple. Charcoal or carbon black has also been used as a black pigment since prehistoric times.

Two of the first synthetic pigments were white lead (basic lead carbonate, (PbCO<sub>3</sub>)<sub>2</sub>)

Pb(OH)<sub>2</sub> and blue frit (Egyptian Blue). While lead is made by combining lead with vinegar (acetic acid, CH<sub>3</sub>COOH) in the presence of CO<sub>2</sub>. Blue frit is a calcium copper silicate and was malacrite. These pigments were used as early as the second millennium BCE.

Many of the Synthetic pigments and dyes such as Prussian blue, Mauveine etc were discovered which were tried on different substrates as synthetic colourants having different hues<sup>[9]</sup>.

## II. Materials and Methods

### Starch Extraction

Cassava and potato were pilled to remove the back, and 500g each were soaked in 5 litres of water and then steeped for 6 hours at room temperature. After steeping, the water was drained and the potato and cassava ground into particles and then sieved in 3 litres of water. The starch extract was allowed to settle in the water for about 2 hours, later the water was separated from the starch by the process of decantation. The starch was dried under the sun for about 3 hours and further ground to fine particles.

### Adsorption Study of Starch Dyeing

The starches (Cassava and Potato), 2g each was dispersed into a dye bath containing different concentrations of the dye from a 2% stock solution. The dyebath, containing from 4 – 24 cm<sup>3</sup> at 4mls interval each was made up to 40mls with the addition of deionised water. Dyeing was carried out in an incubator shaker (agitator, innova 4000) for 24 hours at room temperature. After dyeing, the starch was filtered and washed with about 40 cm<sup>3</sup> of deionised water. The filtrate was further diluted with 500 cm<sup>3</sup> of deionised water, and then absorbance was determined at the λ<sub>max</sub> of the individual dye solutions using UV – visible spectrophotometer.

The absorbance of the dyes before dyeing was also determined using the dilution factor 1:100 while the absorbance of the dye solution diluted (filterates) after dyeing using the dilution factor 1:10, which were designated A<sub>0</sub> and A<sub>1</sub> respectively. The % exhaustion is calculated as:

$$\% E = \frac{A_0 - A_1}{A_0} \times 100\%$$

The same procedure was employed for dyeing with both Reactive Tectilon Blue 4G and Reactive Tectilon Yellow 2G dyes.

### Dye Fixation

Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) solution was prepared using 10g Sodium Carbonate to 500cm<sup>3</sup> by the addition of deionised water. 10cm<sup>3</sup> each of these solutions was added in the dye bath and 2g of the dyed starch each was also added and agitated further for one hour at ambient temperature within which the dye was fixed into the starch. After fixation of the dye, the starch each was filtered and washed thoroughly and allowed to dry and further ground to fine particles.

This procedure was done for both the Reactive Tectilon Blue 4G and Reactive Tectilon Yellow 2G dyed potato and Cassava starch.

### Determination of Optimum Concentration of the Dye.

The optimum concentration of the dye to be used was determined by the adsorption isotherm of each of the dye using the absorbance of the dye before and after dyeing which were designated A<sub>0</sub> and A<sub>1</sub> respectively.

$$\% E = \frac{A_0 - A_1}{A_0} \times 100\%$$

After having determined the percentage exhaustion from 4cm<sup>3</sup> – 24 cm<sup>3</sup> at 4cm<sup>3</sup> intervals each, graphs were plotted in each case using % exhaustion against concentration of the dye. A plateau was determined, which indicated the optimum concentration of the dye.

### Exhaustion

Dye 1.2g and 10g NaCl<sub>2</sub> (common salt) solution was prepared in 200 cm<sup>3</sup> by the addition of deionised water. The starches (cassava and potato) 20gs each were introduced into the dye bath containing the Reactive Tectilon Blue 4G and Reactive Tectilon Yellow 2G dye solutions respectively. Dyeing was carried out in and incubator shaker (agitator) for 24hrs at ambient temperature. After exhaustion the starches were filtered, rinsed and washed thoroughly with deionised water and dried.

### Dye Fixation

Sodium carbonate Na<sub>2</sub>CO<sub>3</sub> (10g), was dissolved in 500 cm<sup>3</sup> of deionised water and 100 cm<sup>3</sup> of this solution was placed in each of the four dyebaths and 20g of the potato and cassava starches each were introduced into the dyebaths and the agitation was carried out in the (agitator) incubator shaker for 30minutes at room

temperature. The starch was then filtered, rinsed and washed with deionised water and finally dried and ground to fine particles.

III. Results and Discussion.

Figure 1 Calibration for the aqueous solutions of the dyes.

The calibration curve for the aqueous solutions of the dyes at concentrations used in all the dyeing experiments indicated that the correlation is very strong being higher than 98%.

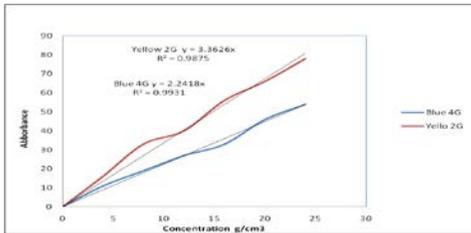


Fig. 1 The Calibration curve of the aqueous solutions of the dyes.

The Exhaustion of the Dyes.

The absorbance readings of the dyes after dyeing (filtrates) for the Reactive Tectilon Blue 4G and Reactive Tectilon Yellow 2G dyed potato and Cassava starches respectively were determined with the U.V visible spectrophotometer using the dilution factor 1:10 (i.e. 1ml dye in 10mls water).

TABLE I. Absorbance of the dye solutions before and after dyeing for the exhaustion data.

Conc g/cm <sup>3</sup>	Reactive Tectilon Blue 4G dyed starch filtrates (Absorbance)			Reactive Tectilon Yellow 2G dyed starch filtrates (Absorbance)		
	Before Dyein g	After dyeing		Before dyeing	After dyeing	
		potat	cassav		potato	cassava
4	11.0	3.8	2.6	16.0	5.0	3.9
8	19.0	4.2	2.5	33.0	6.2	3.9
12	27.0	5.6	3.4	40.0	6.4	5.0
16	33.0	6.2	4.1	56.0	8.6	7.3
20	46.0	7.8	6.9	66.0	9.0	7.6
24	54.0	8.0	7.3	78.0	9.3	8.2

Determination of the Optimum Concentration.

The extracted starch from cassava and potato were dyed with Reactive Tectilon Blue 4G and Reactive Tectilon Yellow 2G dyes to produce Blue and Yellow Pigments. The optimum concentration of the dye was determined from the exhaustion curves of each of the dye shown in figure 2-5. The Plateau shown by the curves indicated the optimum concentration. It was

observed that the optimum concentration of the dye is 0.24g/2g starch.

TABLE II. Exhaustion percentage for Reactive Tectilon Yellow 2G Dye on Potato Starch

Concentration (g/cm <sup>3</sup> )	%Exhaustion
0	0
4	68.5
8	81.0
12	84.0
16	84.6
20	86.3
24	88.0

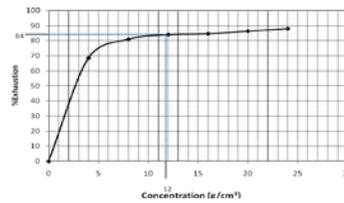


Fig. 2: The Exhaustion curve for Reactive Tectilon Yellow 2G Dye on Potato Starch

TABLE iii: Exhaustion percentage for Reactive Tectilon Yellow 2G Dye on Cassava Starch

Concentration (g/cm <sup>3</sup> )	%Exhaustion
0	0
4	75.9
8	86.5
12	87.5
16	86.9
20	88.4
24	89.4

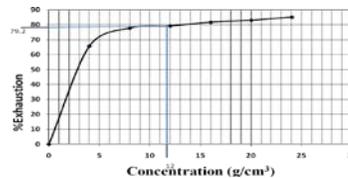


Fig. 3: The Exhaustion curve for Reactive Tectilon Yellow 2G Dye on Cassava Starch

TABLE iv: Exhaustion percentage for Reactive Tectilon Blue 4G Dye on Potato Starch

Concentration (g/cm <sup>3</sup> )	%Exhaustion
0	0
4	65.7
8	77.8
12	79.2
16	81.7
20	83.0
24	85.1

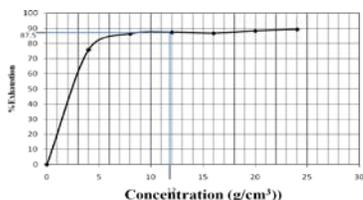


Fig.4: The Exhaustion curve for Reactive Tectilon Blue 4G Dye on Potato Starch

TABLE v: Exhaustion percentage for Reactive Tectilon Blue 4G Dye on Cassava Starch

Concentration (g/cm <sup>3</sup> )	%Exhaustion
0	0
4	76.2
8	86.9
12	87.3
16	87.5
20	85.0
24	86.4

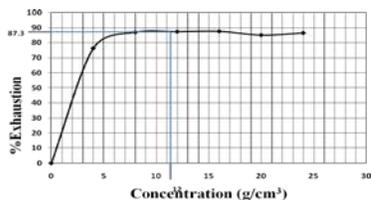


Fig.5: The Exhaustion curve for Reactive Tectilon Blue 4G Dye on Cassava Starch

**Production of the Pigment.**

After having determined the optimum concentrations, starch 20g each were dyed with the two classes of Reactive dyes, using 1.2g dye in 200mls of deionised-water.

A reasonably good yield of pigment was obtained which were found to have brighter colours for both the potato Blue/Yellow, Cassava Blue/Yellow pigments produced respectively. The mass of the starch used was 20g, but after dyeing the mass reduced to 19.5g, which showed that the % yield was about 95%. However, the pigments produced are assumed to have high tinctorial strength owing to the colour obtained

and as there were no blending during filtration and washing.

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