THE EFFECTS OF VANILLIN AS CARRIER IN THE DYEING OF POLYESTER FABRIC

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE DEGREE IN COLOUR CHEMISTRY AND TECHNOLOGY

DEPARTMENT OF POLYMER AND TEXTILE SCIENCE
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APRIL, 2017

DECLARATION

I declare that the work in this dissertation entitled **"THE EFFECTS OF VANILLIN AS CARRIER IN THE DYEING OF POLYESTER FABRIC"** has been carried out by me in the Department of Polymer and Textile Science. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other Institution.

Joseph ODEY	____________	____________
Name of Student	Signature	Date

CERTIFICATION

This dissertation entitled "THE EFFECTS OF VANILLIN IN THE DYEING OF POLYESTER FABRIC" by JOSEPH ODEYmeets the regulations governing the award of the degree of Master of Science in Colour Chemistry and Technology of the Ahmadu Bello University Zaria, and is approved for its contribution to knowledge and literary presentation.

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Member, Supervisory Committee	(Signature)	Date

Prof. Abu S. Lawal

Head of Department	(Signature)	Date

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Dean, School of Postgraduate Studies	(Signature)	Date

DEDICATION

This research work is dedicated to Almighty God,

The one who was, who is, and who is to come,

The fountain of my life.

ACKNOWLEDGEMENTS

I ascribe all glory and honour to Almighty God who has made me undergone this course of study successfully.

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ABSTRACT

The potential use of extracted Vanillin from vanilla flavour for the chemical substitution of toxic carriers used in aqueous dyeing of polyester fabrics was assessed. The extracted vanillin was used to compare the dyeing of a woven polyester fabric with two synthesized azo disperse dye from 2-nitroso-1-naphtol and 1-nitrosol-2-naphthol and two commercial dyes C.I Disperse Yellow 56, and C.I. Disperse Yellow 50. When vanillin and the conventional carriers were used for dyeing at 3% shade at boil, the dye uptakes increased for both vanillin and the conventional carriers but were higher with the conventional carrier especially benzoic acid which gave 81.4% exhaustion and least for salicylic acid which gave 73% exhaustion, at 0.15g of vanillin and pH 4 and70.4% exhaustion for C.I Foron Yellow 50 and least on C.I Disperse Yellow 56 which gave 0.66% exhaustion pH 11. The wash, hot pressing and light fastness were determined, an excellent wash fastness was observed at both ISO2 and ISO3 wash fastness respectively for the conventional carriers and vanillin which gave an excellent rating of 4-5. More so, the light fastness test gives a high fastness rating at an average of 6-7 for both the conventional carrier and vanillin at the different pH and concentration used.The study confirms that vanillin can be used as a chemical substitute to conventional carriers withgood wash and light fastness properties.

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CHAPTER ONE

1.0 INTRODUCTION

In 2009, global production of polyester fibres reached 31.9million tonnes; about 45% ofworldwide fibre production (Oerlikon,2010). Polyester (polyethylene terephthalate (PET)) fibres havea growing importance, and are mainly used in clothing, geotextileand automotive industries. PET has excellent tensile strength andchemical resistance. However as PET is hydrophobic and has nochemically active groups, its dyeing in aqueous conditions is quitedifficult. Dyeing is achieved with disperse dyes having good diffusivityand solubility in PET fibre. Moreover, the highly crystallinestructure of PET fibre slows down the rate of dye diffusion into thefibre(Trotman, 1970).Dyeing of polyester fabrics can be achieved using three differentmethods depending on the quantity of fabrics to be dyed (Dupont,2002).

Thermosol process used for continuous dyeing of thousands of metres of polyester fabrics, is carried out by impregnation of the PET fabric in the dye bathfollowed by squeezing of excess dye bath and then subsequent dried(100-140°C) before dye fixation (at 200-225°C during 12-25sec.). This technique is however restricted to disperse dyes thatcan sublimate and penetrate inside the PET fibre in gaseous state.Thus, only a limited amount of colour shades can be obtained.When special shades are needed, dyeing of polyester fabricswith disperse dyes is achieved usingexhaustion method (deepdyeing)(Dupont,2002). The fabric to be dyed is immersed in the dye bath forlonger period (about 1hr.) under high temperature and pressure,under agitation, with or without addition of a carrier to allow dyediffusion inside the polyester fibre. Exhaustion method is used fordyeing of smaller quantities of polyester fabrics or for dyeing ofpolyester textiles in the form of fibres, yarns or knitted fabrics. Twoexhaust dyeing methods are used: Dyeing under atmosphericconditions (below 100°C) with the aid of carriers and dyeingunder high-temperature and pressure conditions (125-135°C) without carrier. Thelast method is the most commonly applied but it requires highenergy consumption because of high temperature conditions.Carriers are used for dyeing of PET fibres in order to improveadsorption and accelerate diffusion of disperse dyes into the fibre atlow temperature and pressure conditions. Nevertheless, most carriers are toxic e.g. phenol, naphthalene, dicloro benzene, etc., to humans and aquatic organisms (Murray andMortimer,1971). During dyeingand rinsing, a large amount of carriers is released into wastewater,but part remains entrapped in the fibre(Vigo,1994) andis likely to be emitted into air during drying, thermofixation andlater use (e.g. ironing).Chemical carriers include: phenolics, chlorinated aromatics,aromatic hydrocarbons and ether(Vigo, 1994). Some carriers aresaid to be “hydrophobic” and some are “hydrophilic”, and their mode ofaction differ accordingly. Hydrophobic carriers are more effectivethan hydrophilic ones (Burkinshaw,1995). In textile industry, hydrophobiccarriers such as dichloro and trichloro-benzene arealready substituted by hydrophilic carriers such as benzoic acid (Vigo,1994).

1.1 Action of Carriers

During the first stage of dyeing, adsorption of carriers on PETfibre takes place in a manner which is similar to that of dispersedyes. Interactions between PET fibre and carrier involve primarilydispersive forces acting between aromatic parts of the carrier andthe PET polymer (Murray and Mortimer, 1971). As the carrier molecules are smaller in size than the dye molecules,they diffuse more rapidly into the amorphous regions of fibreafter their adsorption onto PET fibre. There is then a swelling of PET fibre and creation of spaces between PET macromolecular chains.Amorphous regions then become more easily accessible to the dyemolecules. This swelling phenomenon causes a plasticization ofPET and therefore a reduction of glass transition temperature Tg(Murray andMortimer, 1971; Vigo, 1994; Burkinshaw, 1995). Thecarrier has thus the effect of accelerating dye diffusion inside PETfibre."Hydrophilic" carriers have a different mode of action: they actas powerful dispersing agent, increasing solubility of the dispersedye inwater, (Burkinshaw, 1995), but their increasedsolubility in water decreases their diffusion inside the PET fibre.Carriers such as phenols have aromatic group which contributes totheir adsorption on the fibre (Balmforth*et al*., 1966).

1.2 Vanillin

Molecular structure of vanillin Fig. 1, is similar to that of traditionalcarriers, which confers to all of them a solubility parameter close tothat of PET. Hence it would be interesting to study the possibleuseof vanillin to substitute traditional toxic carriers.

Naturally occurring vanillin in pods is very expensive and wasfor a long time replaced by petrochemical vanillin for its use in poultry feedsand perfumery, etc. There is nowa great concern for its productionusing biotechnological solution: Rhodia markets biosyntheticvanillin prepared by the action of microorganisms on ferulic acidextracted from rice bran and today lots of research is being undertakento synthesize vanillin from agro-resources such as lignin(McShan, 2005). Moreover, vanillin has antioxidant (Tai *et al*., 2011), antimicrobial and anti-mutagenic effects (Walton *et al*., 2003). In this research, the feasibility of substituting traditional carriersby vanillinis assessed, the fabric is dyed in atmosphericconditions using two differentcommercial disperse dyes having differing molecularweight and two synthesized azo dye. Thepurpose of this study is to assess the feasibility of substitutingtoxic molecules called carriers used for dyeing of polyester fabricsby vanillin from an extracted substance. “Foster Clark” vanilla flavour.

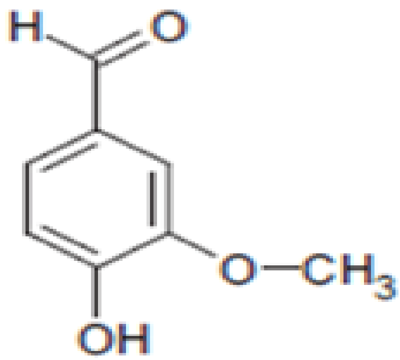


Figure 1: Vanillin structure.

1.3 STATEMENT OF THE RESEARCH PROBLEM

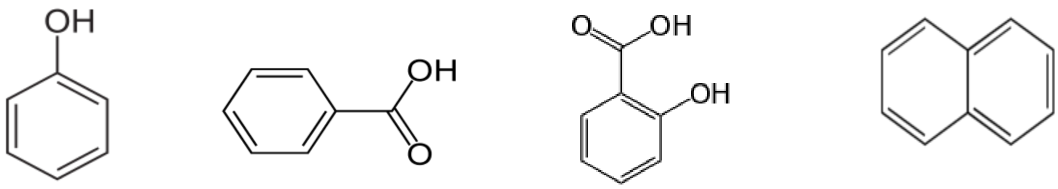
Environmental issues are being increasingly taken into account in textile dyeing and finishing industries because of strict legislations and a growing ecological concern. Main environmental impacts of textile dyeing and finishing industries involve high water consumption, high energy use and also input of a wide range of chemicals (dyes, surfactants, carriers, etc.) Some of these chemicals are hazardous for both human health and environment(Szente*et al.*, 1998). And despite the obvious advantages associated with the chemical carriers in aqueous PETS, dyeing it has a major problem of toxicity on the environment.

Thepurpose of this project is to assess the feasibility of substituting toxic molecules called carriers used for dyeing of polyester fabricswith vanillin whichare environmentally friendly and sometimes less expensive.

1.4 JUSTIFICATION OF THE STUDY

Owing to the toxic nature of the chemical carriers used in the dyeing of polyester fabric, vanillin which is more ecofriendly and with a good solubility nature like the conventional type is used in the dyeing of a woven polyester fabric. Dye uptake was alsocompared to those of traditional carriers such as phenol, benzoic acid,salicyclic acid and naphthalene (Fig. 2 below).

The research seeks to confirm the effect of vanillin as a chemical substitute to traditional carriers and evaluation of wash and light and heat pressing fastness properties.



Phenol Benzoic acid Salicyclic acid Naphthalene

Figure 2:**Chemical Formula of otherCarriers used in the Study**

AIM AND OBJECTIVES

1.5.1 Aim

The aim of this research work is to assess the effect of vanillin as a substitute to the chemical carrier in the dyeing of polyester fabric.

1.5.2 Objectives

The specific objectives of this research include:

i. Extraction of vanillin from vanilla flavour.

ii. Characterization ofthe extracted vanillin using FTIR.

iii. Syntheses of disperse dye from 2-nitroso-1-naphthol and 1-nitroso-2-naphthol

iv. Characterization of the dye using FTIR and UV- visible Spectrophotometre.

v. Assessment of the effect of vanillin on the dyeing of both commercial and synthesized dye on polyester fabric.

vi. Comparison of vanillin with other chemical traditional carriers.

vii. Assessment of pH and concentration on the dye absorption.

viii. Assessment of wash, heat and light fastness properties.

CHAPTER TWO

2.0. LITERATURE REVIEW

2.1 DISPERSE DYES

These are synthetic dyes of low water solubility that in theirdisperse colloidal form are suitable for dyeing and printing on hydrophobic fibres and fabrics. The development of disperse dyes for dyeing secondary cellulose acetate fibres in the early 1920s was a major technological breakthrough although their major use today is for the colouration of polyesters, the most important group of synthetic fibre (Broadbent, 2001). The first systematic study of dyes that was suitable for application to cellulose acetate by a direct dyeing process was carried out by Green in 1924. The presence of hydroxyl and amino groups, a low relative molecular mass and an almost neural or basic character were found to be advantageous. As a result of these investigations, in 1922, Green and Saunders developed the lonamine Dyes (British Dyestuffs Corporation) for application to acetate fibres (Green and Saunders, 1923, Green, 1924). These watersoluble dyes were hydrolysed in the aqueous dye bath to produce the sparingly soluble free base in a very fine suspension that was then absorbed by the fibre. This discovery, that aqueous dispersions of almost water insoluble dyes were highly suitable for the dyeing of secondary acetate, lead to the rapid development of other such dyes for dyeing cellulose acetate. In 1923, aqueous dispersions of dyes were examined independently by the British Celanese Corporation and the British Dyestuffs Corporation and lonamine dyes were superseded by ranges of disperse dyes, such as SRA (British Celanese Corporation) and Duranol (ICI) that were devoid of ionic solubilising groups. These sparingly water-soluble acetate dyes were applied to cellulose acetate in the form a fine aqueous dispersion (Burkinshaw, 1995). The understanding of this mechanism in 1923 initiated the development of genuine disperse dyes. British Celanse and British Dyestuff Corpwere the first companies to introduce these dyes to the market for colouring acetate fibres. These dyes were dispersed with sulphoricinoleic acid, soap or turkey red oil (Fourness, 1979).

The advent of other man-made fibres, such as nylon in 1938 and acrylic in the early 1940s, both of which possess a significant hydrophobic nature, further increased the use of disperse dyes. However, it was the discovery in 1941 and subsequent commercial introduction in 1948, of polyester fibres that triggered an intensive research effort into disperse dyestuffs. Due to the highly crystalline and hydrophobic nature of polyester, the fibre is only slightly swollen by water up to the atmospheric boil which, in the 1950s was the maximum practical temperature available for dyeing. Consequently, new methods of application had to be developed. These new methods involved opening up the fibre structure temporarily so as to facilitate dye penetration (Fourness, 1979).

Disperse dyes are required to be relatively small, planar molecules to allow the dyes to penetrate between the polymer chains and into the bulk of the fibre. These dyes are commonly applied to the fibre as a fine aqueous dispersion at temperatures of around 130 °C under pressure. At these temperatures, the tight physical structure of the polymer is loosened by thermal agitation, which reduces the intermolecular bonding and facilitates entry of the dye molecules. It is essential for disperse dyes to be able to withstand various dyeing conditions, pH and temperature, resulting in negligible changes in shade and fastness (Aspland, 1992 and 1997).

Today, the disperse dyes industry is rated as multi million pound industry, over ninety percent of disperse dyes usage is for the colouration of polyester and its blends (particularly with cellulose). All the major European dye manufacturers market at least one range of disperse dyes (Broadbent, 2001).

2.2 Chemical Constitution Of Disperse Dyes

The majority of disperse dyes are low molecular weight, non-ionic monoazoand anthraquinone derivatives. Polar substituents are usually present in the dye molecule so that the dye has the slight solubility in water required for dyeing. Hydroxyethylamino groups ($NHCH_2CH_2OH$) are typical of such substituent. The interaction of such polar groups with the water, by dipole interactions and hydrogen bonds, is crucial for water solubility. Dipole forces and hydrogen bonds, as well as dispersion forces, also bind the dye molecules to polar groups in the fibres. Approximately 60% of all disperse dyes produced belong to the azo class.(Broadbent, 2001).

2.3 Azo Disperse Dyes

Azo dyes are defined as compounds containing at least one azo group attached to sp^2hybridized carbon atoms, such as benzene, naphthalene, thiazole andthiophene. Under normal conditions, azo dyes exist in the more stable planar transform so that the carbonnitrogen bond angle is approximately 120° (Gordon and Gregory, 1983).Azo dyes represent the largest group of disperse dyes for two reasons;the ease with which an extraordinary number of molecular combinations can be generated by varying the diazo and coupling component, the relatively simple process by which the dyes can be produced. Colours that are less typical of simple azo compounds, such as greenish-yellow and blue are also possible using more specialized components. These may have heterocyclic units or cyanosubstituents.

2.4 DyesAnthraquinone Disperse

Anthraquinone disperse dyes were among the early 'acetate' dyes and have made an important contribution to the violet and blue shade range. They produce bright dyeing of excellent light fastness and cause no dye stability problems during dyeing (Koh, 2011).Anthraquinone disperse dyes are usually 1-hydroxy or 1-amino derivatives. These have bright colours ranging from red through to blue. In comparison of azo dyes with similar shades,anthraquinonederivatives are frequently characterized by greater clarity and better stability against hydrolysis and reduction. Simple anthraquinone dyes have low molar absorptivity compared to azo compounds and therefore give dyeing of lower colour yield. Although anthraquinone disperse dyes have many advantages such as bright shades, high light fastness, good stability in dyeing and excellent levelling, serious economic drawbacks and inevitable population problems ensure the continuing displacement of these dye by other types, such as benzodifuranone dyes and azo dyeshaving heterocyclic diazo components (Griffiths, 1984).

2.5 HYDROPHOBIC FIBRES

Disperse dyes can be applied to a whole range of chemically diverse, hydrophobic man-made fibres, which include acetate, acrylic, modacrylic, nylon, polyester and polyurethanefibres. However, of these, the most important fibres for disperse dyeing are polyester andsecondary cellulose acetate (Aspland, 1997).

2.6 POLYESTER FIBRES

Polyester fibre is a manufactured fibre composed of synthetic linear macromolecules havingin the chain at least 85% (by mass) of an ester of a diol and benzene-1, 4-dicarboxylicacid(terephthalic acid) (Denton and Daniels, 2002). Fibres of the most common polyester,Poly (ethylene terephthalate) (PET) is generally made from either terephthalic acid ordimethyl terephthalate together with ethylene glycol (Fig. 3) (Chalse E. Ophardt,2003)

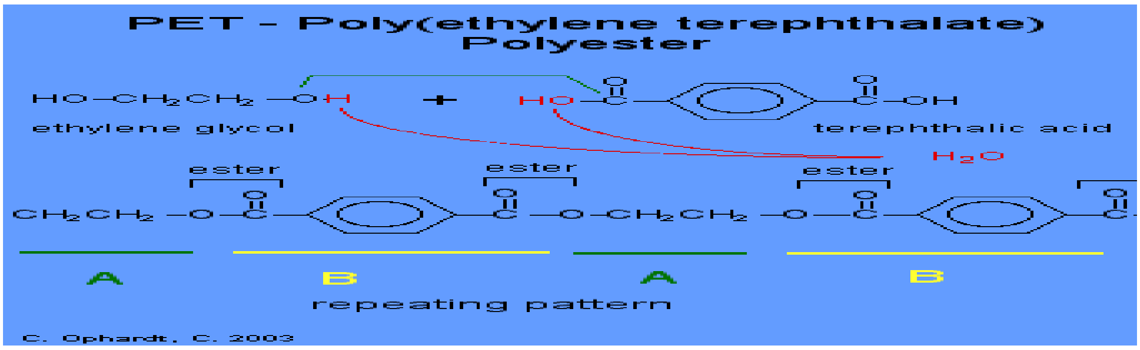


Figure 3. Polymerization of Poly (ethylene terephthalate).

2.7 PROPERTIES OF POLYESTER FIBRES

2.7.1 Physical Properties

Polyester fibres are very hydrophobic, therefore, they absorb only a very small amount ofwater and there is no significant change in their tensile properties when they are wetted.The moisture regain of polyester fibre is approximately 0.4% at 6% relative humidity and20°C. Polyester materials dry quickly because of their very low waterabsorption.The tensile properties of polyester fibres vary with temperature; at 180°C, the fibre retainsapproximately half the tenacity it possesses at room temperature and its extensibilityincreases (Nunn, 1979). Medium-tenacity yarns shrink by approximately 6% in boiling waterbut only by 3% in hot air at the same temperature; similar differences are found at highertemperatures. Polyester fibres will, however, take a permanent-set when distorted at hightemperature.Polyester fibres exhibit high initial moduli of elasticity, high resistance to bendingdeformations and good recovery from them, negligible creep under the low extensions towhich the fibres are most commonly subjected in use and high resistance to abrasion.Polyester can be exposed to sun light for 600 hours and the fibre strength will still be around60-70% of its original strength.

2.7.2 Chemical Properties

Polyester fibres show outstanding resistance to damage by most common chemicals underordinary conditions of exposure and a wide range of substances have little or no effect ontheir strength.Their resistance to oxidizing and reducing agents is excellent and, as a consequence,bleaching treatments using sodium chlorite, sodium hypochlorite or hydrogen peroxidemay be employed. Concentrated formic acid, acetic and oxalic acids produce strength lossesof 15%, 6% and 8%, respectively, after treatment at 80°C for 72 hours, but dilute solutions ofmineral acids are resisted, even at 100°C.Polyester fibres can be treated with dilute alkalis at temperatures up to 100°C and canwithstand the strongly alkaline conditions used in vat-dyeing and or in mercerizing. However, solutions of caustic alkalis do, in fact, attack and hydrolyse the polymer, but attemperatures up to the boil, such attack is confined to the surface of the fibre; this particularcharacteristic has been utilized in the production of silk-like polyester.Polyester polymers display the typical reactions of ester and can be hydrolyzed in thepresence of dilute alkali or acid or by water alone. No serious change can be expected to beobservable in the textile-processing properties of fibres and yarns dyed for one to two hoursat 130°C, so long as the pH of the bath has been maintained close to 7. However, in an acidicbath of pH substantially less than 4 or in an alkaline bath, more rapid attack will occurabove pH 8, high-temperature dyebaths can induce serious degradation of polyester fibresif treatment is prolonged (Nunn, 1979).

2.8 AZO DYES

Azo compounds bearing the functional group R-N=N-R^1, in which R and R^1 can be either arylor alkyl. IUPAC defines azo compounds as: derivatives of diazene(diimide), HN=NH, wherein both hydrogens are substituted by hydrocarbyl groups, e.g.PhN=NPh azo benzene or diphenyldiazene (McNaught and Wilkinson, 1997). By far, azo dye is the largest group of dyes. Azo dye contain at least one azo group (-N=N-) but can contain two (disazo), three (trisazo) or more rarely four (tetrakisazo) or more (polyazo) azo groups. The azo group is attached to two groups of which at least one or more usually, both are aromatic (Hunger, 2003). Azo dyes account for about 60-80% of all organic colourants this is due to their relatively simple synthesis, good technical performance (such as wash, light, perspiration fastness etc) and wide spectrum of colours (Ollgaard*et al.,* 1998).

2.8.1 Method of Synthesizing Azo Dyes

Azo dyes are synthesized exclusively by a two stage reaction sequence of diazotization and azo coupling.

2.8.2 Diazotization

This is the first stage of azo dye synthesis. This first stage is typically performed in the presence of nitrous acid ($HNO_{2)}$, which has been generated in situ with hydrochloric acid (HCl) and sodium nitrite ($NaNO_{2)}$. A primary aromatic amine is used to provide a conjugated system of electrons adjacent to the azo bond that is necessary to colour formation. This primary aromatic amine, known as the “diazo component”, belongs to one of three groups: aniline and substituted anilines, naphthylamines and naphthylaminesulphonic acids (Hunger, 2003).

The overall reaction equation for the diazotisation reaction using sodium nitrite and hydrochloric acid may be given as:

$$ArNH_2 + NaNO_2 + 2HCl \rightarrow ArN_2^+ + Cl^- + H_2O + NaCl$$

The mineral acid of choice for many diazotization is hydrochloric acid. This is because the presence of the chloride ion can exert a catalytic effect on the reaction under appropriate conditions, thus enhancing the reaction rate.

The reaction stoichiometry therefore requires the use of two moles of acid per mole of amine. However, for a number of reactions, a somewhat greater excess of acid is generally used. One reason is that highly acidic conditions favour the generation from nitrous acid of the reactive nitrosating species which are responsible for the reaction. A second reason is that acidic condition suppresses the formation of triazines as side-products which may be formed as a result of N-coupling reactions between the diazonium salts and the aromatic amines from which they are formed (Christie, 2001).

The formed diazoniun salt ($ArN_2^+Cl^-$) is unstable at room temperature, and therefore a low temperature is required for its existence. It is a weak electrophile and will react only with highly electron-rich species, such as amino, hydroxyl and methoxy groups. This highly electron- rich species are known as the "coupling component" (Hunger, 2003).

2.8.3 Coupling

An azo coupling is an organic reaction between a diazonium compound and another aromatic compound that produces an azo compound. In this electrophilic aromatic substitution reaction, the aryl diazoniumcation is the electrophilic aromatic substitution reaction, the aryl diazoniumcation is the electrophile and the active arene is the nucleophile (March, 2007). The most common strong electron-releasing groups are the hydroxyl and the amino groups. Thesecompounds which are capable of undergoing azo coupling are referred toas coupling components. These are either phenols or aromatic amines (primary, secondary, tertiary). Also, a third type of coupling component exist commonly a keto-acid derivative, in which coupling takes place at a reactive methylene group.

To minimise the formation of side products and also to obtain high yield and purity of azo dyes careful control of the experimental conditions is necessary. Temperature control which is of critical essence in diazotization is of less important in coupling. The reaction is carried out at or just below the ambient temperatures (Christie, 2001).

2.8.4 Dyeing Techniques

Disperse dyes are applied by the following techniques:

1. Carrier Dyeing
2. High temperature dyeing
3. Thermosol Dyeing

2.8.5 Carrier Dyeing

The term ‘carrier” dyeing originated from the idea that the compound and the dye formed a complex which could ‘carry’ the dye into the fibre, thus causing more rapid dyeing. It is now known that the carrier is absorbed by the fibre and operates by modifying the structure of the amorphous region (Johnson, 1989).

Neither heavy-depth shades, nor medium depth shades of high fastness to heat treatment can be produced on polyester using apparatus that restricts dyeing temperature to100°C or low without resort to a carrier. A carrier is an organic compound, dissolved or emulsified in the dye bath. Carriers allow dyeing of even deep shades at the boil within a reasonable dyeing time. Thecarrier loosens the inter-polymer bonds and allows the penetration of water insoluble dyes into the fabric (Koh, 2001).

At the end of the dyeing process, the fabric is then washed to remove the carrier molecules. The benefits of carriers were overwhelming in the early days of polyester dyeing. However, carrier dyeing has steadily declined since the development of suitable machinesfor dyeing polyester under pressure at temperature around 130°C. Carriers are still used in some garment and small commission dye houses where high temperature pressurized dyeing machines are not available (Broadbent, 2001).

2.8.6 High Temperature Dyeing

High temperature dyeing is the most widespread method of batch colouration.The temperatures (ca. 130°C) require pressurized equipment and impart increased diffusion of the dyestuff (and therefore increase rate of dyeing) by reducing cohesion between polymer chains and increasing the kinetic energy of the dye molecules (Koh, 2001). A typical exhaust dyeing application sequence for polyester involves three main phases of the process including the heating or adsorption phase, the high temperature or diffusion phase, and the clearing phase.

The heating or adsorption phase is the most critical in determining the levelness of the dyed fibre and it is essential therefore that the heating rate is appropriate to allow controlled adsorption of the dye. The diffusion stage is the rate determining step and the dyeing of polyester is often described as a diffusion-controlled process. This is due to the convective transfer through the liquor adsorption and molecular diffusion into the fibre (Dawson and Todd, 1979). Where the time needed for the adsorption phase is largely influenced by the machine conditions, in the diffusion phase the time required at top temperature is directly related to the diffusion characteristics of individual dyes, dyeing depth, but generally, the standard time is 10-20 minutes for dyeing up to pale shades, 20-30 minutes for medium shades and 30-35 minutes for deep shades.Disperse dyes have such limited solubility in water, some particulate disperse dye may still be occluded on fibre surfaces after the dyeing phase is complete (Aspland, 1997), hence the need for the clearing phase.The usual treatment carried out, especially in heavy depth, is reduction-clearing, where the dyed fibre is treated in a strong reducing bath, usually made up of sodium dithionite and caustic soda. A treatment for 20 minutes at approximately 70-80°C is often sufficient to clear the fibre surface, but the ease of removal varies from chromophore to chromophore and dye to dye. This treatment acts to destroy loose azo disperse dye through chemical reduction of the link (Koh, 2001). In the cases of pale and medium-depth dyeing or for those dyes which cannot withstand reduction-clearing, the dye fibre can be given an alkaline scour residues of anthraquinone dyes which may remain after reduction-clearing, may be removed using an oxidative treatment (Waring and Hallas, 1990).

2.8.7 Thermosol Dyeing

Thermosol dyeing process is an important continuous dyeing process for dyeing polyester and polyester/cellulose fibre mixture with disperse dyes, which is used mainly for woven's and knitted materials (Rouette, 2010). In dyeing polyester fibres, the dyeing time can be shortened significantly by increasing dyeing temperature. The rate of dyeing increases exponentially above the glass transition temperature; a temperature increase of 10°C doubles the rate. For this reason, at 200°C fast coloured fibres can be obtained with disperse dyes within seconds especially for polyester / cellulose mixtures.

This property is used to dye polyester fibres continuously in a pad-fix process, which was introduced by Du Pont as the thermosol process (Broadbent, 2001).

2.8.8 Vanillin

Vanilla was cultivated as flavouring by pre-Columbian Mesoamerican people; at the time of their conquest by Hernán Cortés, the Aztecs used it as a flavouring for chocolate. Europeans became aware of both chocolate and vanilla around 1520. (Esposito*et al*., 1997)

Vanillin was first isolated as a relatively pure substance in 1858 by Nicolas-Theodore Gobley, who obtained it by evaporating a vanilla extract to dryness, and recrystallizing the resulting solids from hot water (Gobley, 1858). In 1874, the German scientists Ferdinand Tiemann and Wilhelm Haarmann deduced its chemical structure, at the same time finding a synthesis for vanillin from coniferin, a glucoside of isoeugenol found in pine bark (Tiemann andHaarmann, 1874).Tiemann and Haarmann founded a company, Haarmann and Reimer (now part of Symrise) and started the first industrial production of vanillin using their process in Holzminden.

Synthetic vanillin became significantly more available in the 1930s, when production from clove oil was supplanted by production from the lignin-containing waste produced by the sulfite pulping process for preparing wood pulp for the paper industry. By 1981, a single pulp and paper mill in Thorold, Ontario supplied 60% of the world market for synthetic vanillin (Hocking,1997). However, subsequent developments in the wood pulp industry have made its lignin wastes less attractive as a raw material for vanillin synthesis. While some vanillin is still made from lignin wastes, most synthetic vanillin is today synthesized in a two-step process from the petrochemical precursors guaiacol and glyoxylic acid (Esposito*et al*., 1997)

Beginning in 2000, Rhodia began marketing biosynthetic vanillin prepared by the action of microorganisms on ferulic acid extracted from rice bran at $700/kg, this product, sold under the trademarked name Rhovanil Natural, is not cost-competitive with petrochemical vanillin, which sells for around $15/kg (Rouhi,2003). However, unlike vanillin synthesized from lignin or guaiacol, it can be labelled as a natural flavouring.

2.8.9 Occurrence

The green seed pods contain vanillin only in its glucoside form, and lack the characteristic odour of vanilla. Vanillin is most prominent as the principal flavour and aroma compound in vanilla. Cured vanilla pods contain about 2% by dry weight vanillin; on cured pods of high quality, relatively pure vanillin may be visible as a white dust or "frost" on the exterior of the pod. At lower concentrations, vanillin contributes to the flavour and aroma profiles of foodstuffs as diverse as olive oil, butter,raspberry, and lycheefruits (Brene *et al*., 1999).Aging in oak barrels imparts vanillin to some wines, vinegar, and spirits (Viriot*et al*., 1993).

In other foods, heat treatment generates vanillin from other chemicals. In this way, vanillin contributes to the flavour and aroma of coffee, maple syrup, and whole-grain products including corn tortillas and oatmeal (Kermasha*et al*., 1995).

2.8.9.1 Natural Production

Natural vanillin is extracted from the seed pods of Vanilla planifola, a vining orchid native to Mexico, but now grown in tropical areas around the globe. Madagascar is presently the largest producer of natural vanillin. As harvested, the green seed pods contain vanillin in the form of its β-D-glycoside; the green pods do not have the flavouror odour of vanilla(Semmelroch*et al*., 1995). After being harvested, their flavour is developed by a months-long curing process, the details of which vary among vanilla-producing regions, but in broad terms it proceeds as follows:

First, the seed pods are blanched in hot water, to arrest the processes of the living plant tissues. Then, for 1–2 weeks, the pods are alternately sunned and sweated: during the day, they are laid out in the sun, and each night, wrapped in cloth and packed in airtight boxes to sweat. During this process, the pods become a dark brown, and enzymes in the pod release vanillin as the free molecule. Finally, the pods are dried and further aged for several months, during which time their flavours further develop. Several methods have been described for curing vanilla in days rather than months, although they have not been widely developed in the natural vanilla industry, (Blank*et al.,* 1992) with its focus on producing a premium product by established methods, rather than on innovations that might alter the product's flavour profile. Vanillin accounts for about 2% of the dry weight of cured vanilla beans, and is the chief among about 200 other flavour compounds found in vanilla.

2.8.9.2 Chemical Synthesis

The demand for vanilla flavouring has long exceeded the supply of vanilla beans. As of 2001, the annual demand for vanillin was 12,000 tons, but only 1800 tons of natural vanillin were produced(Kermasha *et al.,* 1995). The remainder was produced by chemical synthesis. Vanillin was first synthesized from eugenol (found in oil of clove) in 1874–75, less than 20 years after it was first identified and isolated. Vanillin was commercially produced from eugenol until the 1920s (Buttery*et al*., 1995).Later it was synthesized from lignin-containing "brown liquor", a by-product of the sulfite process for making wood pulp. Counter-intuitively, even though it uses waste materials, the lignin process is no longer popular because of environmental concerns, and today most vanillin is produced from the petrochemical raw material guaiacol(Walton, 2003).Several routes exist for synthesizing vanillin from guaiacol(Dignum*et al.*, 2001). At present, the most significant of these is the two-step process practiced by Rhodia since the 1970s, in which guaiacol reacts with glyoxylic acid by electrophilic aromatic substitution. The resulting vanilmandelic acid is then converted to vanillin by oxidative decarboxylation (Gallage*etal.*,2014).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

The chemicals used for this work were of analytical grade mostly from BDH, May and Baker. This chemicals and others where used without further purification. They are as follows: Hydrochloric acid, Potassium hydroxide, Soda, Sodium hydro sulphite, distilled water, Vanilla flavour,1-naphtol, 2-naphthol, Sodium nitrite, Sodium hydroxide, Toluene, Ethanol, Ethanoic acid, Hydrochloric acid, ice block, Phenol, Benzoic acid, Naphthalene, Salisalic acid, C.I. Disperse Yellow 56, C.I.Foron Yellow 50, and two synthesized azo dye.

3.2 Equipment

Spectrophotometer, Micro weighing balance, Thermometer, Magnetic stirrer, Water bath, 50ml and 10ml measuring cylinder, Gallenkamp melting point apparatus, (model: MPD350.BM3.5) Crockmeter,Capillary tube, Retort stand, Volumetric flask, Conical flask, Buckner flask, Filter paper, Stirring rod, UV-visible Spectrophotometer (Model: JENWAY 3405),Separating funnel, Oven.

3.1.1 Extraction of Vanillin

500 mls of artificial vanilla chipsflavour from a commercial Foster Clark's product was transfer into a 250mls separating funnel. This was then extracted using 120 x 4mls of diethyl ether. The solution was shaken vigorously for several minutes, and then the layers were allowed to settle down to separate. The aqueous bottom layer was separated into a beaker, the ether extraction was kept in a round bottom flask. A support distillation panel was set to remove and recover the diethyl ether. At the end of the distillation, a yellowishoil was formed which was transfer into a beaker. The oil was

allowed to settle at room temperature and then it solidifies into a yellowish crystal. This was then allowed to recrystallize below 80°C. The crystal was then allowed to dry overnight and the melting point was determined using Gallen Lamp apparatus (https://www.youtube.com/watch?V=K7ZDSFEsrGg). Retrieved 2015-09-03, 10:18am.

3.1.2 Synthesis of 2–nitroso–1–naphthol Coupling Component

50.03g (0.347 mole) 1–naphthol was dissolved in 500mlsof distilled water containing 8.389g(0.247mol) sodium hydroxide. While vigorously stirring the solution with magnetic stirrer, 68.8mls of ethanoic acid was dropped with the aid of a separating funnel. To the fine suspension produced, 12.14g (0.18mol) sodium nitrite dissolved in 70mls of distilled water was added over an hour using the separating funnel. All reactions were carried out at an ambient temperature. A greenish yellow precipitate product was washed several times with distilled water until a clear filtrate was obtained. This process was repeated several times until the residue was clear golden yellow and then dried in an oven at 60°C and the melting point determined (Ameuru, 2009).

3.1.3 Synthesis of 1–nitroso–2–naphthol

The same procedure as 3.1.2 was followed but just that 2-naphthol was used instead of 1-naphthol.

3.1.4 Diazotisation of 4–nitro aniline

1.38g (0.01mole) 4–Nitro aniline was dissolved in 2mls of hot concentrated HCl, while standing in an ice bath;0.69g(0.01moles)$NaNO_2$ was added over 3 minutes. The solution was kept stirred for a further 45 minutes (Perkins, 1996).

3.1.5 Diazotization of Aniline

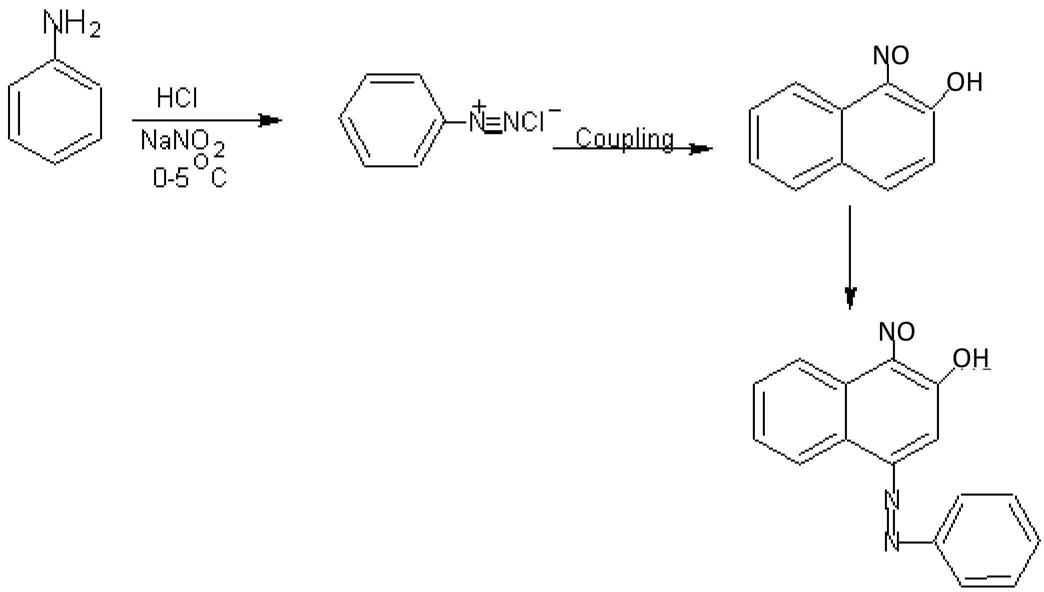
Thesame procedure wascarried out as 3.1.4 above. But just that a direct method of diazotization was carried out here.

3.1.6 General Procedure for Coupling 2-nitroso-1-naphthol

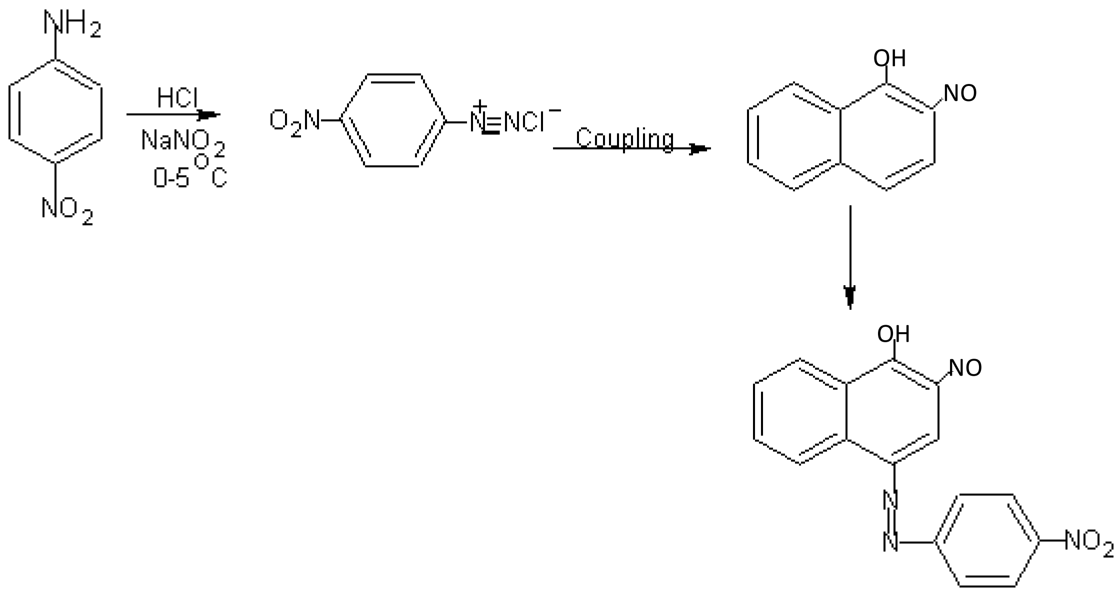
1.72g (0.01 mole) of the 2–nitroso–1–napthol was dissolved in 50mls of distilled water containing 0.4g of NaOH. 50g of crushed ice was added into the beaker standing in an ice salt mixture. The diazoniumsalt of1.38g (0.01mole) 4-nitro aniline was then added gradually to this stirred solution over 30 minutes. The reaction was then allowed to proceed for 1 hour, as shown in scheme 2.(Ameuru, 2009).

3.1.7 General Procedure for Coupling 1–n–2–naphthol

1.72g (0.01 mole) of 1–nitroso–2–naphthol were dissolved in 50mls of distilled water containing 0.4g of NaOH.50g of crushed ice was added into the beaker standing in an ice salt mixture. The diazonium salt(0.01/mole)of aniline was then added gradually to this stirred solution over 30 minutes. The reaction was allowed to proceed for 1 hour, as shown in scheme 1.(Ameuru, 2009).



Scheme 1: Reaction Route for the Synthesis of Dye A.



Scheme 2: Reaction Route for the Synthesis of Dye B.

3.1.8 Percentage Yield

The percentage yield was determined using the formula below:

$$\%yield = \frac{Actual\ yield}{Theorical\ yield} x100 \text{ ---------------------------eq (3.1)}$$

3.1.9 Purification

The synthesized dyes were purified using recrystallization method by dissolving in toluene and heated to boil, then quickly filtered with the aid of suction pump to remove insoluble materials. Further purification was carried out by dissolving the dyes in ethanol and precipitated by addition of distilled water.

3.2 Spectroscopic Analysis of the Dyes and Vanillin

Infrared spectra of the synthesized dyes and vanillin were carried out using FTIR–840DS Fourier transform infrared spectrophotometer.

3.2.1 Ultraviolet–Visible (UV–VIS) Spectroscopic Analysis of Synthesized Dyes

The peak of wavelength of maximum absorption for each dye was determined in ethanol using a Jenwary 6405 UV/Vis spectrophotometre.

3.2.2 Determination of Molar Extinction Coefficient of Synthesized Dyes

The molar extinction coefficient (ε) was carried out by preparing a standard solution of the dyes in ethanol and was calculated using the formula;

$\varepsilon = \frac{A}{Cl}$ ....eq. (3.2)

where;

ε = extinction coefficient,

A = absorbance at λ_{max}

C = concentration of dye in mol/dm^3.

l = path length

3.2.3 Application of the Dyes

The samples1g were dyed in 50 ml beakerswith four different dyes, two (2) commercial (C.I Foron Yellow50 and C.I Disperse Yellow56) and two (2) synthesized azo dyesfrom 2–nitroso–1–naphthol and 1–nitroso–naphthol. For each dyeing the liquor volume was set to 100ml. The amount of each dye used was 3% o.w.fat a liquor ratio of 50:1. The dyeing was carried out at boil for 1 hour at different pH values (4, 5, 7, 9 &11) this was then adjusted using aqueous potassium hydroxide and hydrochloric acid. Then, dyed samples reduction cleared using soda and sodium hydrosulfite for 30 min at 50°C, to remove all physi-sorbed dye molecules on PET fabric surface. At the end, dyed samples was washed twice at 30°C for 10 min in distilled water and dried at room temperature. Dyeing was carried out using vanillin as carrier and results were compared to those of 4 traditional carriers (Giles and Rahman, 1992; Nkeonye, 1987; Miah and Ahmad, 2013).

3.2.4 Reduction Clearing

The dyed materials were treated in a bath containing 1.5g/l dispersing agent, 2g/l caustic soda and 2g/l sodium dithionite at 60°C for 30 minutes. This was aimed at removing unfixed dyes and carrier residues that may be left on the fabric after dyeing (Nkeonye, 1987).

3.2.5 Percentage Dye Exhaustion

The percentage dye exhaustion for each dye was obtained from the dye optical density before dying (OD_1) and the corresponding optical density (OD_2) after dyeing using the 1 cm quartz cells housed in Jenway UV/visible scanning calorimeter at the λ_{max} of each dye, using the expression in eq. 3.3

$$Exhaustion(\%) = \frac{OD_1 - OD_2}{OD_1} \times 100 \text{ ---------------------------------- eq(3.3)}$$

3.3 FASTNESS TEST

3.3.1 Wash Fastness Test

The wash fastness test were carried out using the ISO wash fastness test No2 and 3

Each of the dyed samples of polyester fabric was sandwiched between an undyed cotton and polyester fabrics and subjected to the wash fastness test. The composite specimens were separately agitated in 100ml beaker containing the soap solution, plus other additives as described above under the specified conditions of liquor ratio, temperature and time.The composites specimens were then removed, rinsed and the components separated and dried. The change in colour of the dyed specimens and the staining of the adjacent clothes were assessed with the appropriate grey scale. (ISO 105-AO3: 1987 5th Edition) (Nkeonye, 1987).

3.3.2 Determination of Light Fastness (ISO BOI: 1994)

To test the resistance of a material to fading in day light, samples of polyester dyed fabric were exposed facing due south (in the northern hemisphere), sloping at an angle from the horizontal which is approximately equal to the test site latitude. The samples were covered with glass and provision where made for the samples to be ventilated. Together with the specimen under test, eight standard blue wool cards were exposed. The samples and blue standards were partly covered so that some of the material faded and some left unfaded. A rating is given to the sample which is the number of the reference standard which shows a similar visual contrast between the exposed an unexposed portions as the specimen. The specimen was given a grade rating between one (poor light fastness) and eight (highly resistant to fading) (Saville, 2002).

The samples under test and a set of blue card reference standards are arranged on a suitable backing. The middle third of the strips is covered with opaque card. The assembly was then exposed to light until the specimen just shows a change in shade (4-

5) on the grey scale). The number of the standard showing a similar change was noted. The exposure was again continued until the contrast between the exposed and unexposed parts of the specimen was equal to grey scale 3, at which point the exposure was terminated. When the cards were removed the specimen and standards showed two areas that have been exposed for different lengths of time together with an unexposed area. The specimen was given the rating of the standard which shows similar changes (Saville, 2002).

3.3.3. Determination of Fastness to pressing

Fastness to pressing was carried out under three different conditions, dry, damp or wet:

i. Dry: the specimen was placed on dry undyed cotton adjacent fabric and pressed for 15 seconds with a heated press (a domestic iron was used,) it was assed immediately and after 4 hours interval for colour change and the adjacent fabric for staining.

ii. Damp: the dry specimen was placed on dry cotton adjacent fabric and pressed for 15 seconds. It was then assessed as before.

iii. Wet: the specimen was wetted and placed on dry cotton adjacentfabric and then covered with wet cotton adjacent fabric and pressed for 15 seconds. It was then assed as before (Saville, 2002).

4.0 RESULTS

Table 4.1.1: Structure, Physical and UV- Spectroscopic Properties of the Synthesized,Commercial Dye and extracted Vanillin

Dye	Structure	Molecular weight (g/mol)	Melting point (°C)	Yield (%)	ε =Lmol^{-1}-cm^{-1}x10^{-4}	λmax (nm)

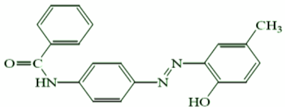
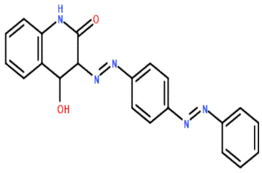
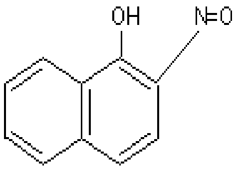
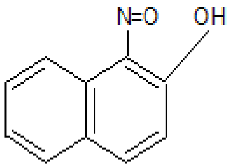
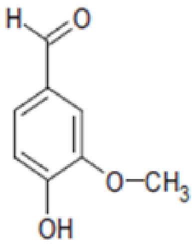
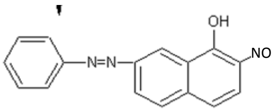
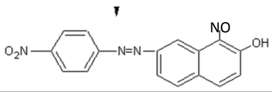
Foron Yellow 50		331.37	□360	-	1.4033	**421**
Disperse Yellow 56		369.38	□360	-	1.4566	**437**
2-nitroso-1 Naphthol		173	154 - 159	-		
1-niroso-2 Naphthol		173	104 - 107	-		
Vanillin		152.15	178-179	78.2		
A		250.11	289-291	74	1.5067	**452**
B		296.11	291-292	84	1.4700	**441**

Table4.1.2: Structures of the Conventional Carriers used

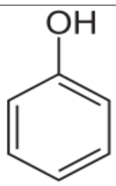
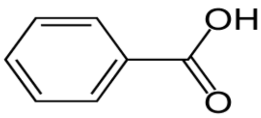
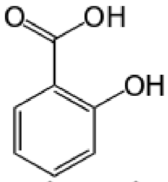
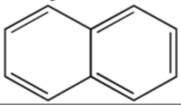
Name	Structure
Phenol	
Benzoic acid	
Salicyclic acid	
Naphthalene	

Table 4.1.3: FT–IR Assessment

Dyes no.	OH Str	C-H Str(aro)	C-H Str(ali)	NO Str	C=C Str	CO Str	C=O	C-N Str	C-C Str	N=N str	N=O
A	3088	1136-1156	-	1174	1486-1574	1031-1093		1067	755.24-848.78	1627-1594	**1574.99**
B	3223.08-3356.07	969.20-1109.58	-	1289.68	1518.68-1647.17	1009.58-1079.72	-	1079.72	852.10	1592.82	**1592.82**
Vanillin	3173	1154-1200	1300	-	1509-1558	1028	1772	-	812.56	-	
1-nitroso-2-naphthol	3309.9	-	-	-	-	-	1066-1259				**1530.7**
2-nitroso-1-naphthol	3190.6	-	-	-	-	--	-	-	-		**1550.6**

Table 4.1.4: Exhaustion (%) for the Conventional Carrier

Carriers	Conventional carriers		Dye A		DYE B	
	C.I ForonYellow 50	C.IDisperse Yellow 56	pH 4	pH 7	pH 4	pH7
Naphthalene	75	7.4	48	40	46	12
Phenol	71	37	61.3	56	54.5	20.7
Salicylic acid	73	6.6	58	54.4	64.6	38.4
Benzoic acid	81.4	16	51.7	48.3	55.5	50

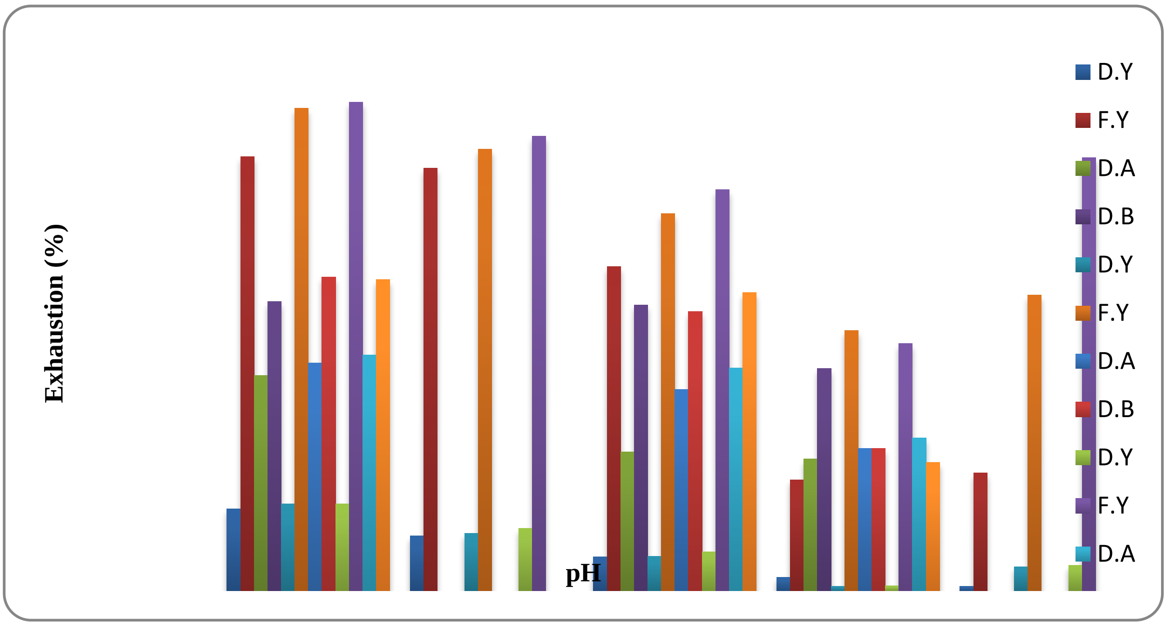


Figure4: Percentage Exhaustion on Samples using Vanillin

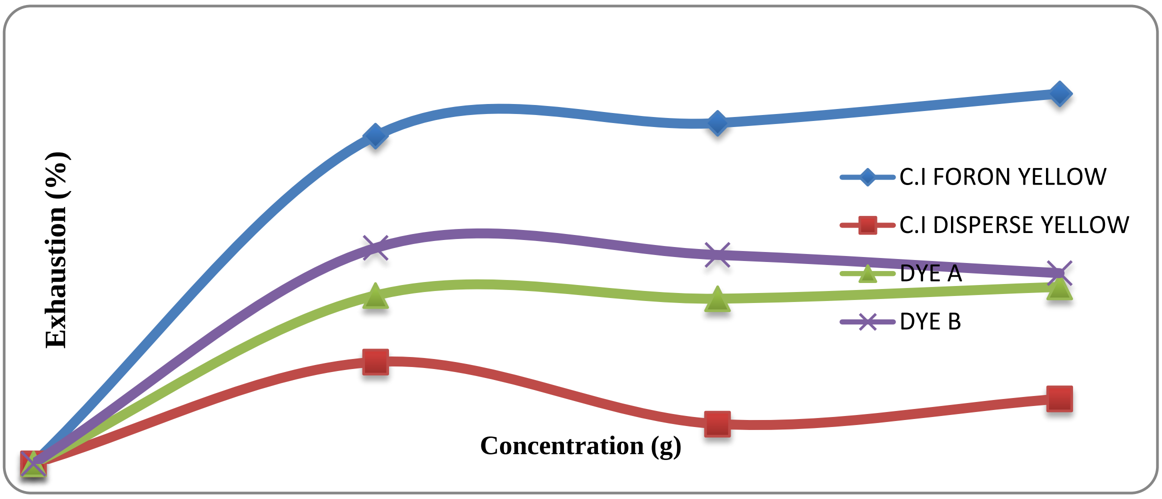


Figure 5: Effects of Concentration on Exhaustion Percentage Using Vanillin

Table 4.1.5: ISO 2 Wash fastness for Disperse Yellow 56 using Vanillin

	0.05 g		0.1 g		0.15 g	
pH	**Change in Shade**	**Staining of Adjacent fabric**	**Change in Shade**	**Staining of Adjacent fabric**	**Change in Shade**	**Staining of Adjacent fabric**
4	4-5	4-5	4-5	4-5	4-5	4-5
5	5	5	4-5	4-5	4-5	4-5
7	5	5	5	5	5	5
9	5	5	5	5	5	4-5
11	5	5	5	5	4-5	5

where: 1= Poor, 2= Fair, 3= Good, 4= Very good, and 5= Excellent

Table 4.1.6: ISO3 Wash Fastness for Disperse Yellow 56 using Vanillin

	0.05 g		0.01 g		0.15 g	
pH	**Change in shade**	**Stainingof Adjacent Fabric**	**Change in Shade**	**Staining of Adjacent Fabric**	**Change in Shade**	**Staining of Adjacent Fabric**
4	4-5	4-5	4-5	4-5	4-5	4-5
5	4-5	4-5	4-5	4-5	4-5	4-5
7	4-5	4-5	4-5	4-5	4-5	4-5
9	4-5	4-5	4-5	4-5	4-5	4-5
11	4-5	4-5	4-5	4-5	4-5	4-5

where: 1= Poor, 2= Fair, 3= Good, 4= Very good, and 5= Excellent

Table 4.1.7: IS0 2 Wash Fastness for C.I Foron Yellow 50 Using Vanillin

pH	0.05g Change in shade	Staining of adjacent fabric	0.1g Change in shade	Staining of adjacent fabric	0.15g Change in shade	Staining of adjacent fabric
4	4-5	4-5	4-5	5	4-5	4-5
5	4-5	4-5	4-5	4-5	4-5	4-5
7	4-5	5	5	4-5	4	5
9	4-5	4-5	4-5	4	4	5
11	5	4-5	4-5	5	4-5	4-5

where: 1= Poor, 2= Fair, 3= Good, 4= Very good, and 5= Excellent

Table 4.1.8: ISO3Wash Fastness for Foron Yellow 50 using Vanillin

	0.05 g		0.01 g		0.15 g	
pH	**Change in shade**	**Stainingof Adjacent Fabric**	**Change in Shade**	**Staining of Adjacent Fabric**	**Change in Shade**	**Staining of Adjacent Fabric**
4	4-5	4-5	4-5	4-5	4-5	4-5
5	4-5	4-5	4-5	4-5	4-5	4-5
7	4-5	4-5	4-5	5	4-5	4-5
9	4-5	4-5	4-5	5	4-5	4-5
11	4-5	5	4-5	4-5	4-5	4-5

where: 1= Poor, 2= Fair, 3= Good, 4= Very good, and 5= Excellent

Table 4.1.9: IS0 2 Wash Fastness for Conventional Carriers

	C.I.Foron Yellow 50		C.IDisperse Yellow 56	
Carrier	**Change in Shade**	**Staining of Adjacent Fabric**	**Change in Shade**	**Staining of Adjacent Fabric**
Benzoic acid	4–5	4-5	4–5	4-5
Naphthalene	4–5	4-5	4–5	4-5
Phenol	4–5	4-5	4–5	4-5
Salicyclic acid	4	4	4-5	5
No carrier	3	3	3	3

where: 1= Poor, 2= Fair, 3= Good, 4= Very good, and 5= Excellent

Table4.2.0: IS03 Wash Fastness for Conventional Carriers

Carrier	C.I.Foron Yellow50		C.I.Disperse Yellow 56	
	Changein Shade	Staining of Adjacent Fabric	Changein Shade	Staining of Adjacent Fabric
Benzoic acid	4	4-5	4–5	4-5
Naphthalene	4–5	4-5	4–5	4-5
Phenol	4	4	5	5
Salicyclic acid	4	4	4-5	4-5
No carrier	3	3	3	3

where: 1= Poor, 2= Fair, 3= Good, 4= Very good, and 5= Excellent

Table 4.2.1: IS0 2 Wash Fastness for Neutral Vanillin

	Foron Yellow 50		Disperse Yellow 56	
Grams (g)	**Change in Shade**	**Staining of Adjacent Fabric**	**Change in Shade**	**Staining of Adjacent Fabric**
0.05	4	4	4–5	5
0.10	4–5	4-5	4	4-5
0.15	4–5	4-5	4–5	4-5

Table4.2.2: IS03 Wash Fastness for Neutral Vanillin

C.I Foron Yellow 50			C.I. Disperse Yellow 56	
Grams	**Changein Shade**	**Staining of Adjacent Fabric**	**Changein Shade**	**Staining of Adjacent Fabric**
0.05	5	5	5	5
0.10	4	4-5	4–5	4-5
0.15	4–5	4-5	4–5	4-5

Table 4.2.3: ISO2 Wash Fastness for Synthesized Dye A Using Vanillin

0.05g			0.1g	
pH	**Change in shade**	**Staining of adjacent fabric**	**Change in shade**	**Staining of adjacent fabric**
4	4	4	4	4
7	4	4	4	4
9	4–5	4-5	4	4

where: 1= Poor, 2= Fair, 3= Good, 4= Very good, and 5= Excellent

Table 4.2.4: ISO3 Wash Fastness for Synthesized Dye A Using Vanillin.

	0.05g		0.1g	
pH	**Change in shade**	**Staining of adjacent fabric**	**Change in shade**	**Staining of adjacent fabric**
4	4–5	4-5	4–5	4-5
7	4	4	4	4-5
9	4	4	4	5

Table4.2.5: ISO2 Wash Fastness for Synthesized Dye B Using Vanillin

0.05g0.1g				
pH	**Change in shade**	**Staining of adjacent fabric**	**Change in shade**	**Staining of adjacent fabric**
4	4–5	4-5	4	4
7	4	4	4	4
9	4	4	4	4

Table 4.2.6: ISO3 Wash Fastness for Synthesized Dye B Using Vanillin

	0.05g		0.1g	
pH	**Change in shade**	**Staining of adjacent fabric**	**Change in shade**	**Staining of adjacent fabric**
4	4	4	4–5	4-5
7	4	4-5	4-5	5
9	4–5	4-5	4	4

Table4.2.7:ISO2 Wash Fastness on Conventional Carrier used on Synthesized Dye A

Carrier	pH	Change in Shade	Staining
Phenol	4	4-5	5
Phenol	7	4-5	5
Benzoic Acid	4	4-5	4-5
Benzoic acid	7	4-5	4-5
Naphthalene	4	4-5	4-5
Naphthalene	7	4-5	4-5
Salicyclic Acid	4	4-5	4
Salicyclic Acid	7	4-5	5

where: 1= Poor, 2= Fair, 3= Good, 4= Very good, and 5= Excellent

Table 4.2.8:ISO3 Wash Fastness on Conventional Carrier used on Synthesized Dye A

Carrier	pH	Change in Shade	Staining of Adjacent
Phenol	4	5	5
Phenol	7	4-5	4-5
Benzoic acid	4	4-5	5
Benzoic acid	7	4-5	5
Salicyclic acid	4	4-5	4-5
Salicyclic acid	7	4-5	4-5
Napthelene	4	4-5	5
Napthelene	7	4-5	4-5

Table 4.2.9: ISO2 Wash fastness on Conventional Carrier used on Synthesized Dye B

Carrier	pH	Change in Shade	Staining of Adjacent
Phenol	4	5	4-5
Phenol	7	4-5	4-5
Benzoic acid	4	4-5	4
Benzoic acid	7	4-5	4-5
Salicyclic acid	4	4-5	4-5
Salicyclic acid	7	4-5	4
Napthelene	4	4-5	4
Napthelene	7	4-5	4-5

Table 4.3.0: ISO3 Wash Fastness on Conventional Carrier used on Synthesized Dye B

Carrier	pH	Change in Shade	Staining of Adjacent
Phenol	4	4	4-5
Phenol	7	4-5	4-5
Benzoic acid	4	4-5	4
Benzoic acid	7	4-5	4-5
Salicyclic acid	4	4	4-5
Salicyclic acid	7	4-5	4
Napthalene	4	4-5	4
Napthalene	7	4-5	4-5

where: 1= Poor, 2= Fair, 3= Good, 4= Very good, and 5= Excellent

Table 4.3.1: Light Fastness for Disperse Yellow 56

	0.05g	0.1g	0.15g
pH	**Light Fading**	**Light Fading**	**Light Fading**
4	6	7	6
5	7	5	6
7	5	6	5
9	6	6	6
11	5	7	6

Key:

1= Poor, 2= Slight, 3= Moderate, 4= Fair, 5= Good, 6= Very good, 7= Outstanding, 8= Excellent.

Table4.3.2: Light Fastness for C.IForon Yellow 50 Using Vanillin

	0.05g0.1g	0.15 g	
pH	**Light Fading**	**Light Fading**	**Light Fading**
4	6	6	5
5	6	7	6
7	6	5	6
9	5	7	7
11	6	7	6

Key:

1= Poor, 2= Slight, 3= Moderate, 4= Fair, 5= Good, 6= Very good, 7= Outstanding, 8= Excellent.

Table 4.3.3: Light Fastness for Conventional Carrier Dyed Samples

Carriers	FY LF	DY LF	DA LF	DB LF
Benzoic acid	4	5	6	5
Naphthalene	5	6	6	6
phenol	5	5	5	7
Salicylic acid	4	6	6	6
No carrier	7	7	8	7

Where: FY= FORON YELLOW, DY=DISPERSE YELLOW, DA= DYE A, DB= DYE B, LF=LIGHT FADING

1= Poor, 2= Slight, 3= Moderate, 4= Fair, 5= Good, 6= Very good, 7= Outstanding, 8= Excellent.

Table4.3.4: Light Fastness for Neutral Vanillin

g	Foron Yellow light Fading	Disperse Yellow light Fading
0.05	7	6
0.1	6	7
0.15	6	6

Table4.3.5: Light Fastness for Synthesized Dye A and B.

PH	0.05g DYE A	0.1g DYE A	0.05g DYE B	0.1g DYE B
4	6	7	6	6
7	7	7	6	7
9	6	6	7	7

Key:

1= Poor, 2= Slight, 3= Moderate, 4= Fair, 5= Good, 6= Very good, 7= Outstanding, 8= Excellent.

Table 4.3.6: Fastness to Hot Pressing for the Commercial Dyed Sample

	DRY				DAMP				WET			
	FY		DY		FY		DY		FY		DY	
PH	CS	DS	CS	DS	CS	DS	CS	DS	CS	DS	CS	DS
4	4	4	4	4	4-5	5	4-5	5	4-5	4-5	4-5	5
5	4-5	4-5	4-5	4-5	4	4	4	4	4-5	4-5	4-5	4-5
7	4-5	4-5	4	4	5	5	4-5	4-5	4	4	5	5
9	4-5	4-5	5	5	4	4	5	5	4	4	4-5	4-5
11	4	4-5	5	5	4-5	4-5	4-5	4-5	4-5	5	4-5	4-5

where: CS= change in shade, DS= degree of staining of adjacent fabric, FY= Foron Yellow 50,DY = disperse Yellow 56
1= Poor, 2=Fair, 3= Good, 4= Very good, and 5=Excellent

Table 4.3.7: Fastness to Hot Pressing on Vanillin Dyed Samples

	DRY				DAMP				WET			
	DA		DB		DADB				DA		DB	
pH	CS	DS	CS	DB	CS	DS	CS	DS	CS	DS	CS	DS
4	4-5	5	5	5	4-5	5	5	5	4-5	4-5	4-5	5
7	4-5	4-5	5	4-5	5	5	4-5	4-5	4-5	4-5	5	5
9	4-5	4-5	5	5	5	4-5	5	5	4-5	4-5	4-5	4-5

Table 4.3.8: Fastness to Hot Pressing For Conventional Carriers at Dry

Carriers	F.Y		D.Y		D.A		D.B	
	CS	DS	CS	DS	CS	DS	CS	DS
Benzoic acid	4-5	4-5	4-5	5	4-5	4-5	4-5	5
Naphthalene	4-5	4-5	5	5	5	4-5	4-5	4-5
Phenol	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Salicylic acid	4	4	5	4-5	5	5	5	5
No carrier	4	4	3	3	4-5	4	4-5	4-5

Table4.3.9: Fastness to Hot Pressing on Conventional Carriers Dyed Samples at Damp

	F.Y		D.Y		D.A		D.B	
Carriers	**CS**	**DS**	**CS**	**DS**	**CS**	**DS**	**CS**	**DS**
Benzoic acid	5	5	4-5	4-5	4-5	4-5	4-5	5
Naphthalene	4-5	4-5	5	5	5	4-5	4-5	4-5
Phenol	4-5	4-5	4-5	4-5	5	5	4-5	4-5
Salicylic acid	4-5	4-5	5	4-5	4-5	4-5	5	5
No carrier	5	5	4-5	4-5	4	4	4-5	4-5

Table 4.4.0: Fastness to Hot Pressing using Conventional Carriers at Wet

	F.Y		**D.Y**		**D.A**		**D.B**	
Carriers	**CS**	**DS**	**CS**	**DS**	**CS**	**DS**	**CS**	**DS**
Benzoic acid	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
Naphthalene	4-5	4-5	5	4-5	4-5	4-5	4-5	4-5
Phenol	5	5	4-5	4-5	4-5	4-5	4-5	4-5
Salicylic acid	4-5	4-5	5	4-5	4-5	4-5	4-5	4-5
No carrier	4-5	4-5	4-5	4-5	5	5	4-5	4-5

CHAPTER FIVE

5.0 RESULTS AND DISCUSSION

5.1 ASSESSMENT OF FT-IR ABSORPTION SPECTROSCOPIC PROPERTIES

The IR spectra in general show characteristic broad band peaks for dye A at 3088cm^{-1} indicating the presence of O-H, C-H at 1136-1156 cm$^{-1,}$ 1174 cm^{-1} due to NO, 1486-1574 cm^{-1} due to C=C stretch, 1031-1093cm^{-1} due to CO stretch, 1627-1594 cm^{-1} due toN=N stretch, while dye B shows peak at 3223.08-3356 cm^{-1} due to OH groups, 1289.68 cm^{-1} due to NO stretch, 1518-1647 cm^{-1} due to C=C stretch, 1009 - 1079 cm^{-1} due to CO groups, 1079 cm^{-1} due to C-N stretch, 1592 cm^{-1} due to N=N groups. The vanillin shows OH at 3173 cm^{-1}, C-H aromatic at 1154-1200 cm^{-1}, C-H aromatic at 1300 cm^{-1}, C=C at 1509-1558 cm^{-1}, CO stretch at 1028 cm^{-1}, C=0 at 1772 cm^{-1}, also the 1-nitroso-2-napthol shows peak at 3309 cm^{-1} for OH, C=O at 1066-1259 cm^{-1}, N=O at 1330 cm^{-1}, the 2-nitroso-1-napthol shows at OH at 3190 cm^{-1}, N=O at 1550 cm^{-1}. As seen in Table 4.1.3.

5.2 Physical Characteristics of the Dyes and Vanillin

The physical characteristics of the dyes and vanillin were shown in Table 4.1.1., each possessed distinctive physical characteristics. The dyes exhibited well defined melting points. This shows that the values were quite high and ranged between 289, 291, >360 and 178- 179 for dye A, B, commercial dyes and vanillin respectively. As compared to literature values for other set of disperse dyes and vanillin. This could be due to difference in molecular structure of the dye in literature compared to the synthesized dyes and extracted vanillin although no attempt was made to discuss detail of individual melting point of the dyes because of complex dependence of melting point on a number of factors like polarity, size, geometry, and etc (Choi *et al.,* 2013). The colour of the synthesized dye and commercial dyes were golden yellow and brownish yellow respectively,while the vanillin is white in colour.

5.2.1 Visible Absorption Spectra of the Dyes

Visible absorption spectra data of the synthesised dyes were measured and recorded by the use of JENWAY 6405 UV/VIS Spectrophotometre. This was measured in ethanol which was shown in table 4.1. The maximum molarextinctioncoefficients (ε) were calculated by the Beer-Lamberts law. The wavelength of maximum absorbance (λ_{max}) range of the synthesised dyes were 452 - 441 nm and 421 - 437nm for the commercial dyes, all within the visible region as shown in Table 4.1.1.The high absorbance value of the dyes could be correlated in terms of substituent effect of the group in azo disperse dyes (Ghoneim*et al*., 2008).

5.2.2 Effects of pH on Dye Exhaustion

Fig. 4shows the effect of pHon the dyeing exhaustion of the synthesized and commercial dye respectively. It was observed that there was an increased in dyeing exhaustion at acidic medium and then subsequent decrease as it approaches basicity. The resultsshows a higher percentage exhaustion when the Foron Yellow 50 was used than the dispersed Yellow 56, this result may be attributed to the facts thatdye having the solubility parameter close to that of the polymer would have high exhaustion (Karst *et al*., 2007). This further proves that the effect of carrier on dye exhaustion is greatly dependent on the nature of the dye and the pH used (Yang and Huda, 2003). Also the synthesized dye B and A show similar character on approaching basicity at the given concentration although dye B gives the highest percentage exhaustion.Also the percentage exhaustion without pHcontrol using vanillin was also assessed, Table 4.1.6

shows a higherpercentage exhaustion when the C.I.Foron Yellow 50 was used to compare with the C.I Disperse Yellow. Thisresult shows that at high pH values, electrostatic repulsion between negatively charged PET, and negatively charged dye and vanillin, would make dye adsorption more difficult and would thus decrease the dye uptake (Pasquet *et al*., 2012). This is one of the reasons why PETS fibre are dyed on commercial scale around this low pH region. However, alkaline pH is detrimental to the intergrity of this fibres. In alkaline region polyesters fibres are hydrolyzed.

5.2.3 Effect of Carrier Concentration on Dye Exhaustion

The carrier concentrations were varied from 0.05g, 0.1g and 0.15g, it was observed that as the carrier concentrations increases, dye exhaustion also increases, as shown in Fig. 5. The reason is based on the fact that carrier is a swelling agent, when added to the dye baths, it swell the fibre, thereby increasing the size of the fibre pores and accelerating the rate of diffusion of the molecules into the fibre (Nkeonye, 1987). Also this swelling phenomenon causes a plasticization of PET and therefore a reduction of glass transition temperature Tg (Murray and Mortimer, 1971; Vigo, 1994; Burkinshaw, 1995).The overall highest exhaustions were obtained usingC.I Foron Yellow50 at 81.4% using benzoic acid, Table 4.1.4. The amount of carrier increased the amount of dye inside the fibre to a certain value (Burkinshaw, 1995).While the least exhaustion was recorded with the Disperse Yellow used,which may be due to the high molecular size of the dye (Lee and Kim, 1998).

5.2.4 Comparison of conventional Carriers and Vanillin

Both vanillin and the conventional carriers gives an increase in the percentage exhaustion, but the conventional carriers gives the highest exhaustion value all through, but does not increase noticeably on increasing the concentration. This results shows that the conventional carriers have a closer solubility parameter with that of the PETS fibre and does not have high solubility nature with the water molecule. Penetration of carrier molecules in PET will depend on the solubility of the carrier in the PET (Tavanaie, 2010). Higher solubility of the vanillin and their diffusion into the PET will be reduced due to their increased affinity with respect to water molecule in the dye bath.

5.2.5 Assessment of Wash Fastness

The resistance of dyed materials to laundry treatment is referred to as wash fastness. This is very important and there are several washing tests that are applied according to the purpose to which the material is intend to be used.In this work ISO wash fastness No. 2 and 3 were used to determine the wash fastness of the dyed polyester material. The ratings vary from good to very good for the C.I.Disperse Yellow56 at 0.05 g, 0.1 g and 0.15g vanillin, at pH 4, 5, 6, 7, 9, and 11 respectively, which shows a very good result. While the ISO No. 2wash fastness for the disperse dye shows an excellent result at 0.05 under the same pH condition. The rating of very good was observed for the ISO No. 2 and 3wash fastness for theC.I.Foron Yellow 50 as shown in Table 4.1.7 and 4.1.8 at the samepHand vanillin concentration used. On using the conventional carrier as shown in table 4.2.0 using ISO wash fastness No 3,a very good result was obtained for both C.I.ForonYellow 50 and C.I.Dispersed Yellow 56. But when no carrier was employed a fair result was obtained. Furthermore,ISO No. 3 and 2 wash fastness was employed on neutral vanillin without pH control asshown in Tables 4.2.1 and 4.2.2 at concentration 0.05g, 0.1g and 0.15g, an excellent to very good result was obtained for both the Foron Yellow 50 and Disperse Yellow. Moreso, the ISO No. 3and 2 wash fastness were used on the synthesized dye A and B as shown in Tables 4.2.3 – 2.2.6, at two different concentrations; 0.05g, 0.10g and at pH 4, 7, and

9. The results obtained ranges from good to very good. While the assessment of the conventional carriers was done on dye A andB forpH 4 and 7 respectively as shown in Table 4.2.7-4.3.0., the result obtained were all very good. The fastnessresults obtained are almost the same, whatever the pH used. This excellent result could be as a result of increase in size and polarity of the dye molecule which reduces it mobility within the fibre and so reflected in a lower diffusion coefficient and an attendant increase in wash fastness.

5.2.6 Assessment of Light Fastness.

As can be seen from Tables 4.3.1 to4.3.5 thereis generally goodlight fastness for both C.I. Disperse Yellow 56 and Foron Yellow 50 and the dye A and B respectively ranging from 5 to 7, this could be as a result of the inherent photo stability of the dye molecule, the concentrations of the dye within the fibre, usually the fastness of the dye fibre increases with increasing the dye concentrations, also it could be as a result of the incident radiation, not all the absorption are equally effective in starting a fading process. Also it could be as a result of the composition of the atmosphere, the moisture content of the atmosphere can have a marked effect on the fading rates of certain dyes (Giles, 1974).

5.2.7 Fastness to Heat Pressing

Heat Pressing fastness can be an important property of disperse-dye on polyester, because of the use of heat treatments in the finishing of the fabric. Disperse dyes are not chemically combined with the fibre/fabric, but are mechanically held in solid solution. Thus, when they undergo the influence of heat they are free to vaporise out of the fibre with little or no decomposition (Hauser, 2011).

Tables 4.3.6-4.4.0show the results of fastness to heat pressing on the polyester fabrics respectively. The results show that both the commercial and the synthesised dyes had very good to excellent heat pressing.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECONMENDATIONS

6.1 SUMMARY

The effects of vanillin in the dyeing of polyester fibre using two commercial dyes, C.I.Foron Yellow 50, and C.I Disperse Yellow 56 and two synthesised azo dyes in comparison with the conventional carriers has been investigated and reported in this research work. The aim of the research was to assess the effects of vanillin as a substitute to the conventional carrier in the dyeing of polyester fabric. Other specific objectives achieved were, to extract vanillin from a vanilla flavor, to characterize the extracted vanillin using FTIR, to synthesized disperse dye from 2-nitroso-1-naphthol and 1-nitroso-2-naphthol, to characterized the dyes using FTIR and UV- visible Spectrophotometer, to apply and assess the dyes using vanillin as carriers on the polyester fabric, to compare vanillin with other chemical traditional carriers based on pH, concentrations and dye absorption, and to assess wash fastness, light fastness and heat pressing of the dyed fabrics.

The dyes were successfully applied on the polyester fabric using both the conventional carrier and the vanillin as the non-conventional carrier.The melting point of all the synthesized dyes and intermediates were determined using Gallenkamp melting point apparatus. The synthesized dyes were found to melt within the range of 289-291°C, while that of vanillin was within the range of 178- 179°C. The wavelengths of maximum absorbance were determined using Visible spectrophotometer in ethanol solvent. The dyes absorbed within the visible region of 441-452 nm. The molar extinction coefficients of all the synthesized dyes were very high which indicates high tinctorial strength of the dye. On application of the dyes onto the fabrics, both the commercial and the synthesized dyes attained a degree of exhaustion on polyester fabric with the highest exhaustion on using the C.I.Foron Yellow 50. The FTIR analysis of the synthesized dyes and intermediate, using FTIRmachine, SHIMADZU model at range of 4000-400 cm^{-1} revealed the basic functional groups that identified the intermediates, dyes and vanillin.

Carrier method of dyeing was employed at liquor ratio of 50:1, percentage shade of 3% at a boil for periods of one hour.Wash fastness, light fastness and heat fastness were fully examined and evaluated on the dyed fabric. Based on this assessment, most of the dyes were found to have an average mean rating of 4-5 for change in colour and degree of staining of adjacent white fabric. This indicates a high fastness to washing, pressing respectively. Lastly, the dyes when subjected to light fastness test were found to have an average good to excellent fastness ratings ofbetween5 to 7.

6.2 CONCLUSION

Conventional carriers having high toxicity are gradually being replaced by other processes, which are not always environmentallyfriendly. This study was carried out to study the potential use of an extracted vanillin molecule for substituting carriers used for polyester fabric dyeing process. Increased disperse dye uptake was observed at acidic condition when both vanillin and the conventional carriers were used using both the commercial and the synthesised dye, but higher for C.I. Foron Yellow 50 and least for C.I. Disperse Yellow 56 dyes. The experiments showed that both vanillin and the chemical carriers allowed a uniform distribution of the various disperse dyes in thepolyester fibre. The dye exhaustion was slightly higher when the chemical carriers were used than the vanillin, but both hadgood to excellent wash, light, and heat fastness. There was an increase in the dye uptake as the concentration of the vanillin increases.The study also confirms that dyeing withvanillin can be carried out at neutral pH without addition of other chemicals to adjust pH. The study confirms that vanillin can substitute conventional carriers used in the dyeing of polyester fabric.

6.3 RECOMMENDATION

The use of vanillin can also be assessed on other class of disperse dyes such as in the anthraquinone group.

6.4 CONTRIBUTIONS TO KNOWLEDGE.

i. At the end of the research it was successfully affirmed that vanillin can be extracted from the locally available vanilla flavour.
ii. Vanillin can serve as carriers in dyeing polyester fabrics
iii. Dyeing using vanillin can best be done at pH range of 4-7 if so wished or done without pH control to achieve excellent result.

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APPENDIX I

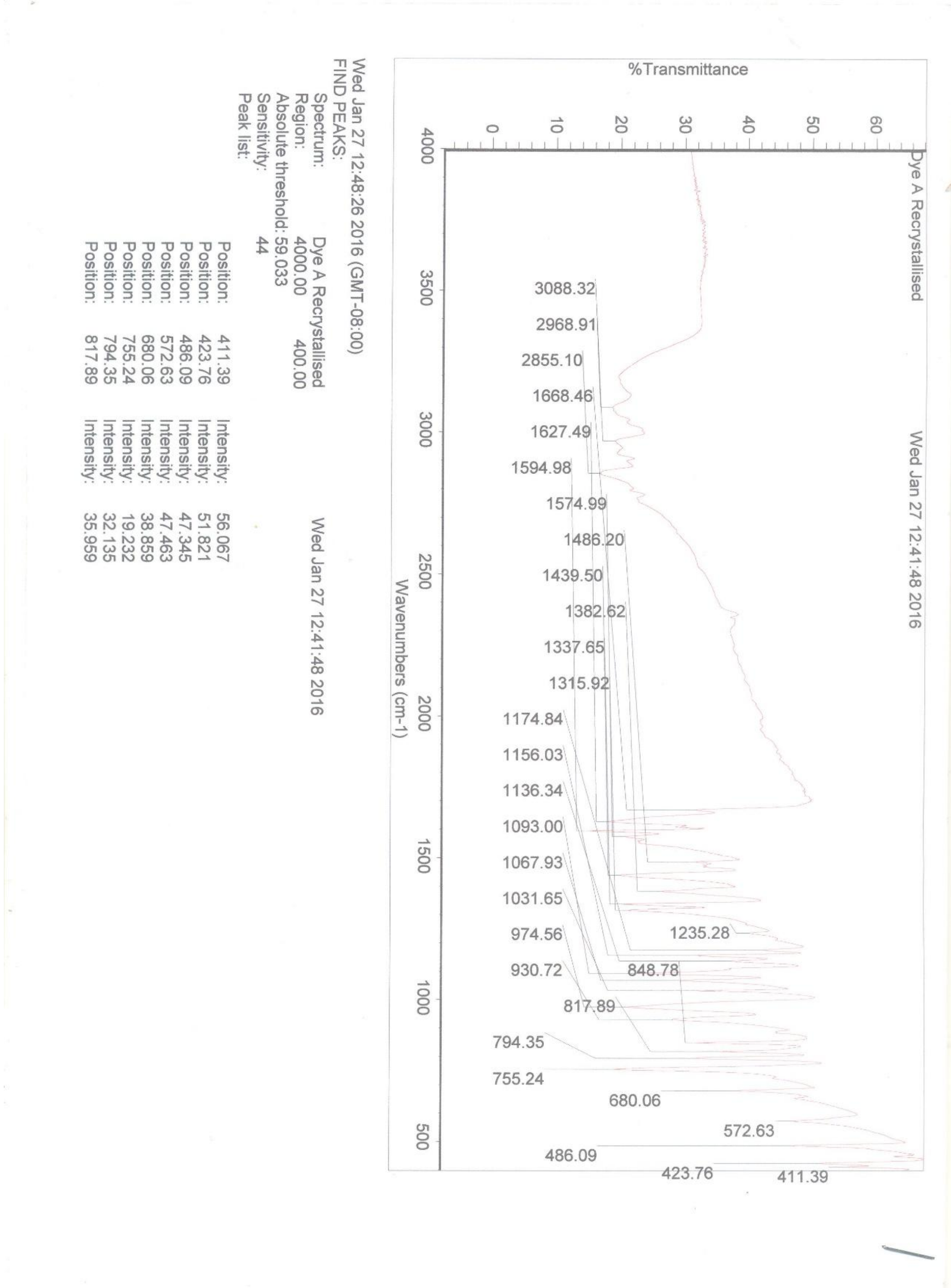

Fig. 6: FTIR Spectrum of Dye A.

APPENDIX II

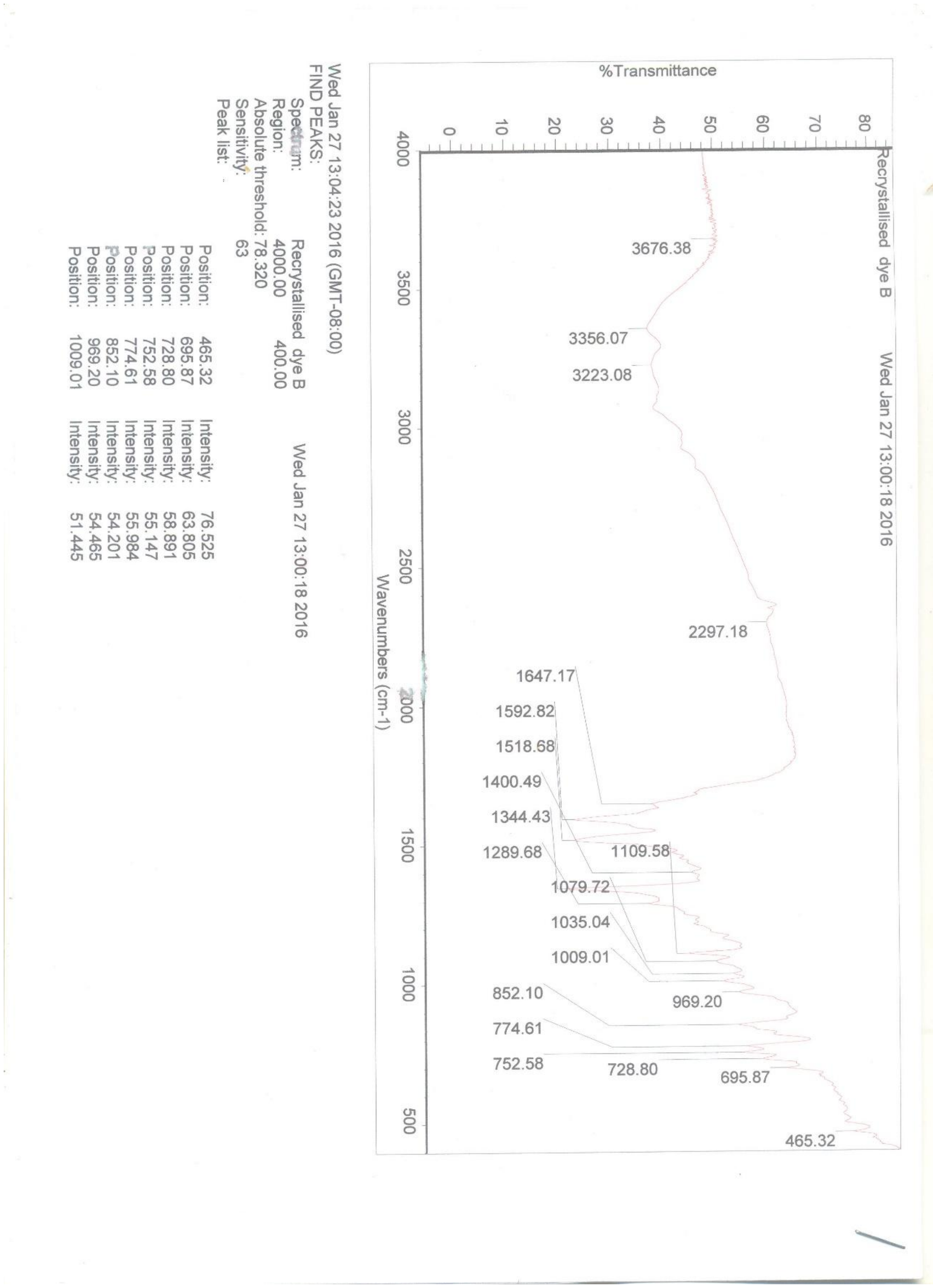

Fig. 7: FTIRSpectrum of Dye B.

APPENDIX III

Agilent Technologies

Sample ID:SYNTHESIZED 2- NITROSO -1- NAPTHOL

Method Name:Transmittance Method

Sample Scans:16

User:Admin

Background Scans:16

Date/Time:2016-03-30T09:36:15.862+01:00

Resolution:8

Range:4000 - 650

System Status:Good

Apodization:Happ-Genzel

File Location:C:\Program Files\Agilent\MicroLab PC\Results\SYNTHESIZED 2- NITROSO -1- NAPTHOL _2016-03-30T09-36-15.a2r

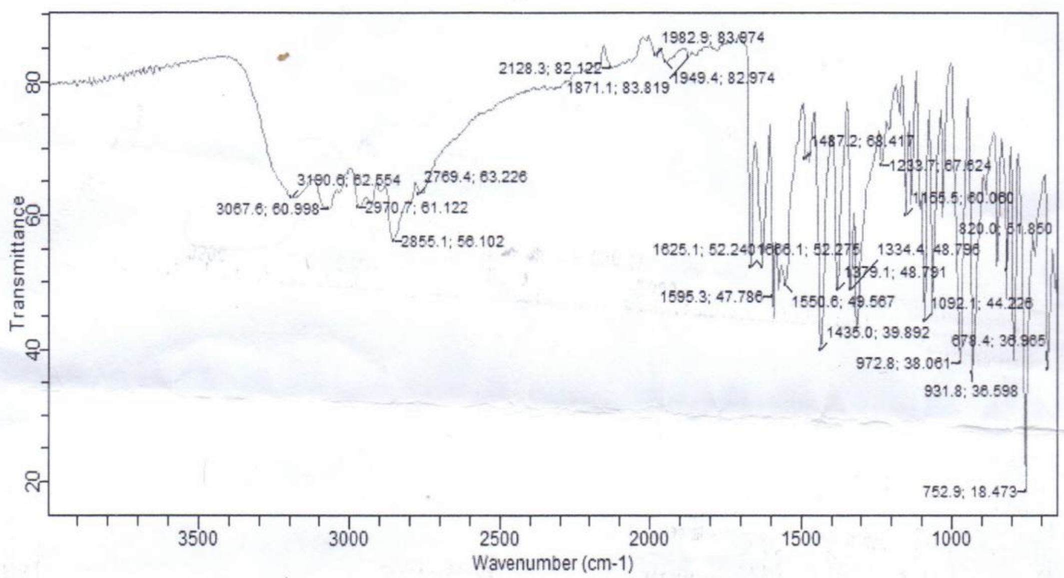

Fig. 7: FTIR Spectrum of 2-nitroso-1-naphthol.

APPENDIX IV

Agilent Technologies

Sample ID:SYNTHESIZED 1- NITROSO -2-NAPTHOL
Method Name:Transmittance Method
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User:Admin
Background Scans:16
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Resolution:8
Range:4000 - 650
System Status:Good
Apodization:Happ-Genzel
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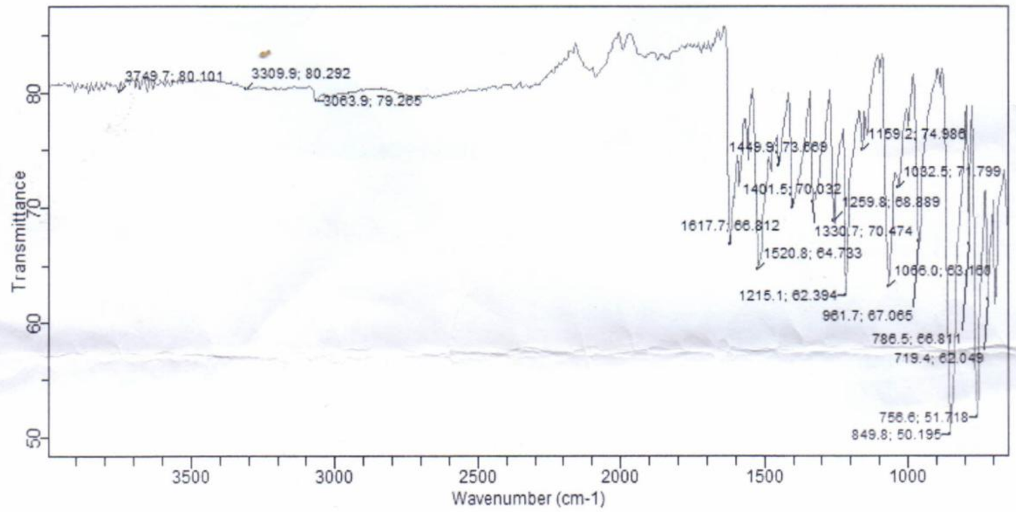

Fig. 7: FTIR Spectrum of 1-nitroso-2-naphthol.

APPENDIX V

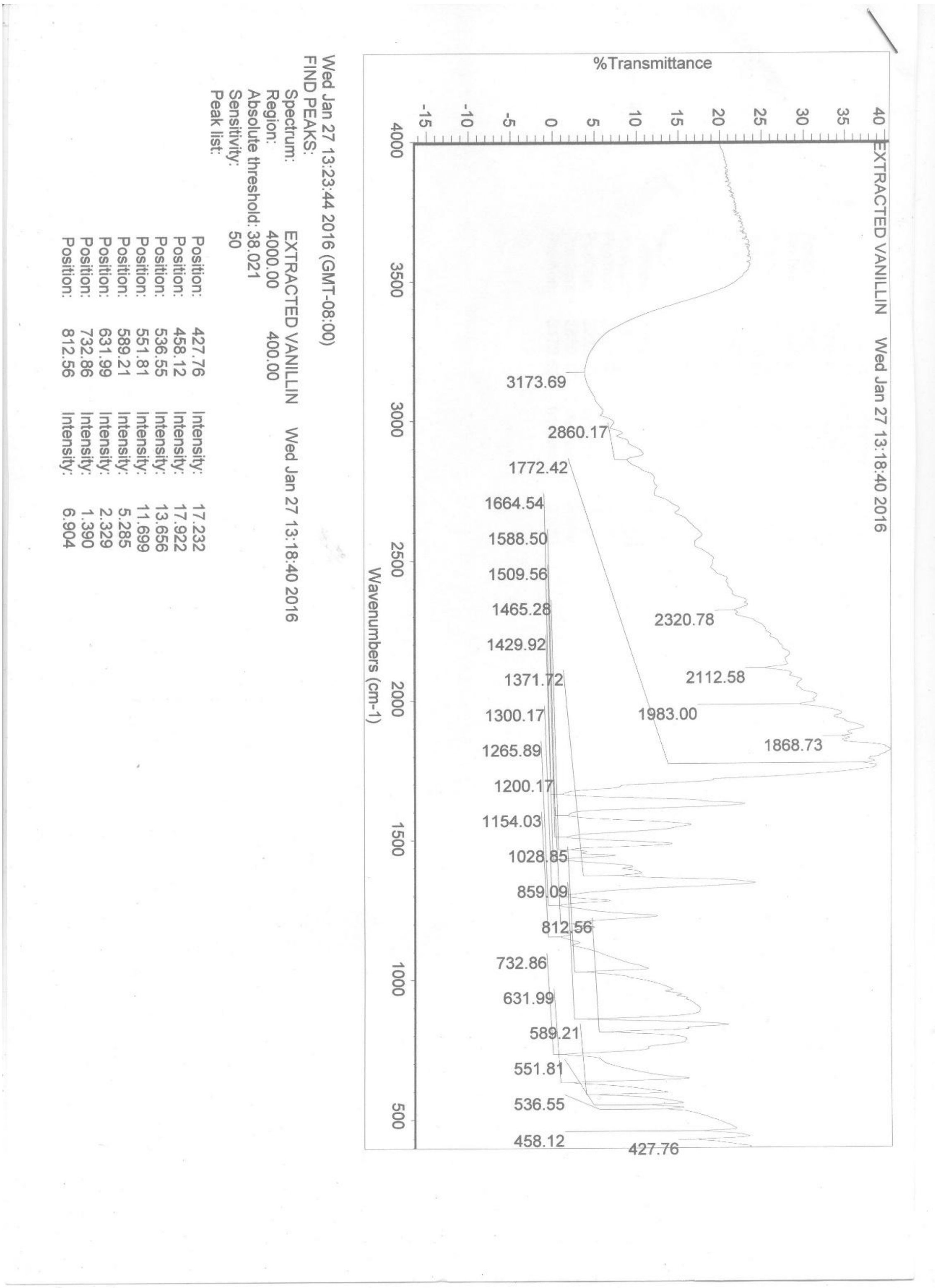

Fig. 7: FTIR Spectrum of Extracted Vanillin.

APPENDIX VI

Plate I: Dyed fabric samples.

APPENDIX V

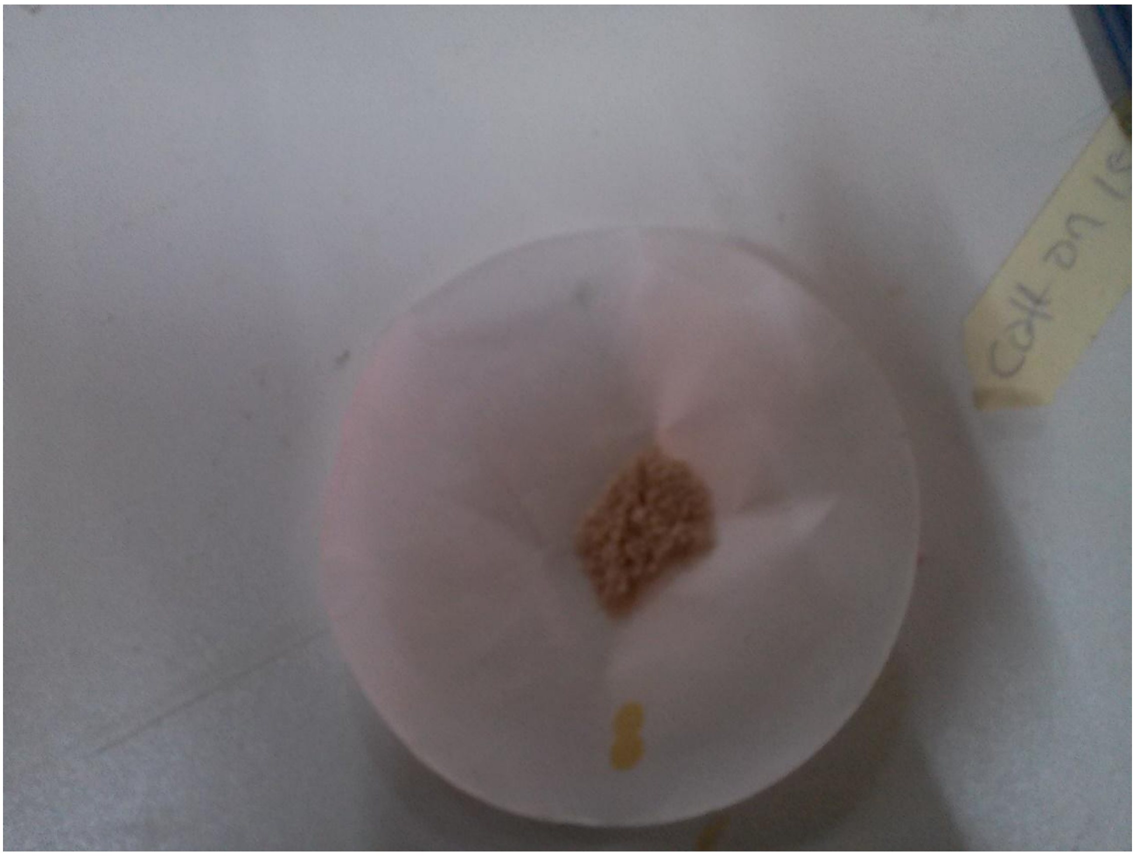

Plate II: Extracted vanillin.

Appendix VI

Table 4.1.5 Exhaustion percentage using Vanillin.

pH	0.05				0.10				0.15			
	D.Y	**F.Y**	**D.A**	**D.B**	**D.Y**	**F.Y**	**D.A**	**D.B**	**D.Y**	**F.Y**	**D.A**	**D.B**
4	11.8	62.5	31	41.7	12.5	69.5	32.8	45.2	12.5	70.4	34.0	44.8
5	7.9	60.9	-	-	8.3	63.6	-	-	9.0	65.5	-	-
7	4.9	46.7	20	41.2	5.0	54.3	29	40.2	5.6	57.8	32.1	43
9	1.98	16	19	32	0.66	37.5	20.5	20.5	0.7	35.6	22.0	18.5
11	0.66	17	-	-	3.5	42.6	-	-	3.7	62.4	-	-

where: DY= Disperse Yellow 56, FY= Foron Yellow 50, DA= Dye A, DB= Dye B

Appendix vii

Table 4.1.6: Exhaustion (%) of Vanillin on Dye A, B, and Commercial Dye without pH Control

Concentration (g)	C.I FORON YELLOW 50	C.I DISPERSE YELLOW 56	DYE A	DYE B
0.05	61.2	19	31.4	40.3
0.10	63.6	7.4	30.8	39
0.15	69.1	12.1	33	35.6