STUDIES ON THE WRINKLE RESISTANCE AND WASHING FASTNESS PROPERTIES OF COTTON FABRICS USING CROSS-LINKED VINYL POLYMERS.

BY

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DECEMBER, 2015.

DECLARATION

I hereby declare that this work is the product of my research efforts undertaken under the supervision of Prof. S. M. Gumel and has not been presented elsewhere for the award of a degree or certificate.

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CERTIFICATION

This is to certify that the research work for this dissertation and the subsequent preparation by hussaini salihi with registration number SPS/12/CHM/00031 were carried out under my supervision.

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APPROVAL PAGE

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DEDICATION

This work is dedicated to my father late Alhaji Salihi Umar Agaisa and my mother late Hajiya Zainab Adamu, (May their souls rest in perfect peace. Ameen).

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CHAPTER FIVE

LIST OF ABBREVIATION

FAA; Untreated yellow dyed fabric.

FAB; Yellow dyed fabric treated with poly (vinyl alcohol).

FAC; Yellow dyed fabric treated with poly (vinyl butyral).

FBA; Untreated brown dyed fabric.

FBB; Brown dyed fabric treated with poly (vinyl alcohol).

FBC; Brown dyed fabric treated with poly (vinyl butyral).

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ABSTRACT

Cross-linked poly (vinyl alcohol) and poly (vinyl butyral) (produced from the reaction of PVA and PVB with urea, respectively) were used as a wrinkle/crease resistance finish and as after-treatment of cotton dyed with direct dyes. The specimens were subjected into different treatments such as fastness tests, crease/wrinkle resistance test, wear and abrasion resistance test and tensile strength test, in which the fabrics treated with cross-linked polyvinyl alcohol showed better washing fastness than those treated with cross-linked poly (vinyl butyral), whereas those treated with cross-linked PVB showed better light fastness than those treated with cross-linked PVA. In terms of mechanical properties like wrinkle/crease resistance, tensile strength and wear and abrasion resistance tests, those fabrics treated with cross-linked PVB showed better improvements.

CHAPTER ONE

1.0. INTRODUCTION.

Cotton is a natural fiber composed mainly of cellulose. The cellulose chains are composed of micro fibrils which have only hydrogen bonds between them. This means there are no covalent cross links to force the cellulose chains to return to their original position when deformed by wrinkling or laundering. Therefore, the goal in wrinkle-resistance treatment of cotton fabrics is to achieve a smooth appearing fabric that will not crease after laundering. Formaldehyde-based resins were used for such treatments but usually ended up losing the strengths of the fabrics. (A. C. S., 2004).

This has become the major aim of the textile industry to come up with a wrinkle free treatment that does not cause the fabric to loss strength. But according to John, (2004), the end of all, is to do the finishing without at least altering the strength and the wear resistance of the cotton fabric. This is one of the main reasons why cotton is blended with various synthetic fibers.

Direct dyes, on the other hand, are water soluble dyestuffs which are absorbed directly by cellulosic fibers e.g. cotton. The introduction of direct dyes opened a new era in cotton dyeing, making the production of wide variety of shades possible at low cost. The generally poor wet fastness of direct dyes is a great technical defect, for which it is necessary to improvise means of improving. (Nkeonye, 1987).

Burkinshaw & Kumar (2009) reported an after treatment with polyvinyl alcohol found to improve the fastness of three direct dyes on cotton to washing at 60^0C. The effectiveness of the after treatment was enhanced by the sequential application of an organic titanate, $MgSO_4$, and 3 different protease enzymes. This was attributed to the formation of a large molecular size, low-water solubility complex situated at the surface of the dyed substrate which physically resists diffusion of the dye from the dyed fabric during washing.

1.1. CHEMICALLY MODIFIED POLY VINYL ALCOHOL.

Fernandez *et al.* 2006. Studied the condensation reaction of butyraldehyde with poly (vinyl alcohol), which give poly (vinyl butyral) using N-methyl-2-pyrrolidone (NMP). The acetalisation reaction under a variety of conditions gave at best a polymer with 97% acetalisation. The ratio of acetal units from meso and racemic dyads of PVA were determined by ^{1}H-NMR. The acetalisation degree was reflected in the solubility of PVB, all products were soluble in NMP. PVBs were characterized by IR Spectroscopy, ^{1}H and ^{13}C NMR.

Busuguma (2010) studied the use of cross-linked polyvinyl alcohol as a finish and after treatment of direct dyes on cotton fabrics. The treatments generally showed improvements in properties like washing and light fastness, mechanical properties like tensile strength, crease recovery angle and wear and abrasion resistance properties.

George *et al* (1959). Work on imparting crease resistance and crease retention to cotton with APO (tris (1-Aziridinyl) Phosphine Oxide). The treatment made the cotton to be crease resistant. An after treatment with a 1% primenitus solution increased the crease recovery angle.

Olivera & Karinstana (2010) Studied the differences between cotton and viscose fibers cross-linked with BTCA (1,2,3,4-butane tetra carboxylic acid) on crease/wrinkle resistance property. The cross-linkage increases wrinkle resistance and reduces the mechanical properties.

Kamal (1971). Reported the use of carboxymethylated cotton cross-linked with triazin derivative to study crease resistance on cotton, the treatments gave products which are superior in hand, abrasion resistance and in most physical properties, compared with the unmodified cotton cloth given the same reagents treatments. Variation of reagents concentration showed that the carboxymethylated cotton had higher capacity for the crease-proofing reagent and exhibited much less change in hand than the unmodified cloth with equivalent amount of reagents.

1.2. AIM OF THE RESEARCH.

The aim of this research work is;

To investigate the effect of some vinyl polymers on improving fastness properties wrinkle/crease resistance of dyed cotton fabrics.

1.3. OBJECTIVES OF THE RESEARCH.

The objectives of the research are;

1. To chemically cross link poly (vinyl alcohol) and poly (vinyl butyral) with urea.
2. To dye the cotton with direct dyes.
3. To use cross linked poly (vinyl alcohol) and poly (vinyl butyral) as after-treatment for Direct dyes on cotton fabrics.
4. To also apply the cross linked poly (vinyl alcohol) and poly (vinyl butyral) as finish, for wrinkle/crease resistance of cotton fabrics.
5. To investigate the change of the properties of the dyed cotton fabrics.

CHAPTER TWO

2.0. LITERITURE REVIEW.

2.1. COTTON.

Cotton is a cellulose fiber (plant derived) from the seedpod of cotton plant. It is widely used for all apparel for its comfort characteristics. The comfort of cotton is due to its absorbency.

Cotton's exact age is unknown. Scientists have found pieces of cotton cloth in caves in Mexico that are at least 7,000 years old. Cotton was grown and made into cloth in the Indus river Valley in Pakistan as early as 3,000 years before the birth of Christ. Egyptians were also weaving cotton fabrics around the same time. Cotton arrived in Europe, through Arab merchants; in approximately 800 A.D. cotton eventually replaced flax and wool as Europe leading choice of fabrics. Columbs found cotton in the Bahama island in 1492. Cotton was known all over the world by 1500.

Presently, cotton is the world most used fiber. Every part of the cotton plant is useful. The fiber is the most important part of the plant because it is used in making cloths. Cotton is the number one fiber used for apparel in the United States. In 1994, 63 percent of cotton was used for apparel, 29 percent for home furnishings and 8 percent was used for industrial type products and exportation (Saara, & Anna, 2009).

2.1.1. PROPERTIES OF COTTON.

Cotton is a natural fiber composed mainly of cellulose. The cellulose chains are composed of micro fibrils which have only hydrogen bonds between them. Cotton garments are superior in comport to those made from synthetic fibers, due to greater moisture regain and absorptivity.

2.1.2. WRINKLING/CREASING AND SHRINKING OF COTTON FABRICS.

During wearing and cleaning, fabrics are temporarily distorted to accommodate the stress of use. If the fabric does not recover its original shape, the results are described as “wrinkling”. Untreated cotton fibers do not have a permanent memory. The cellulose chains in the fiber move by breaking and re-establishing hydrogen bonds. There are no natural forces to promote the cellulose chains to return to their original configuration (Kandolph *et al.,* 1993).

Cotton wrinkles easily when worn, it shrinks after first wash then gradually from every wash after and it does not recover well from stretching. However, cottons appearance-retention properties can be greatly improved by the type of finish that is applied, the fabric type, the fiber is made from and by the fiber it is blended with. For cotton it’s all about the fabric and finish (Berkley, 1942).

Cotton shrinkage is as a result of its structure and the way it is spun, woven and finished. At the fiber level, a study was done to determine the shrinkage of cotton as a result of its structure, specifically looking at the primary and secondary walls. The experiment concluded that with or without the secondary wall, cotton does not swell back to its original length after drying, no matter the swelling agent. Then, when the fiber is spun into yarn its aptitude of shrinking will be enhanced (Berkley, 1942).

2.1.4. DYEING OF COTTON.

The objective of dyeing is to obtain uniformly dyed fabric to the desired colour with the required fastness properties. In dyeing process, the dye molecule first is transferred from the dye liquor to the substrate, it then adsorbed by the substrate (cotton) and then diffused into the substrate. Dyeing of cotton and other cellulosic fibers with Direct dyes is carried out in neutral or mildly alkaline bath with addition of common salt or sodium sulphate at temperature near boiling (Sharma, 2011).

2.1.5. FINISHING OF FABRICS.

Finishing of fabric is one of the most important of fabric processing.

It provides a means of modifying the fabric properties without changing the fiber composition. Thus, a fiber can be standardized for its best all-around properties and finishing relied upon to change the fabric properties for the particular end use desired. Furthermore, it is often the only way in which many of these properties can be obtained. (Reeves, 2007).

Fabric finishing, as the name implies, is the last processing to which the fabric is subjected. It is designed to impart a specific property or properties to the fabric. The fabric may be mechanically finished such as by being heat set, or sanforized, or the finishing may involve the addition of chemicals such as water repellents or resins. Resins are a group of sticky, liquid, organic substances that usually harden, upon exposure to air, into brittle, amorphous, solid substances (Cooke & Roth, 1956).

The finishing materials are usually applied to the fabric from an aqueous solution, dispersion or emulsion by immersing the fabric and then passing it through squeeze rolls to remove the excess liquor. The fabric is then dried and cured at higher temperature if the finishing materials require curing. Industries have been applying finishes to both synthetic and natural fibers that are used to manufacture garments, for many years (Cooke & Roth, 1956).

Finishes can provide fibers with crease resistance wrinkle resistance, or a durable press finish. The durable press finish, is often called a permanent press or wash and wear finish. These finishes are typically provided by various resin materials and can both desirably or undesirably alter the final characteristics of the finished textile. Crease resistance finishes are used on cotton, rayon and linen to prevent wrinkling. Resin finishes are applied to these textiles with processes that involve saturating the textile with the resin and then curing the resin at a temperature of about 182^0C (Logue & Hall, 1994).

2.1.6. CREASE/ WRINKLE RESISTANCE OF COTTON.

One of the most important fabric properties for wearing apparel is resistance to wrinkling. Most of the synthetic, hydrophobic fibers inherently are more resistant to wrinkling than the natural fibers such as cotton, wool, rayon, especially under the condition of high humidity. The ability of a fabric to recover from wrinkling is determined primarily by its elastic recovery from deformation. This elastic recovery may be immediate and complete, in which case the wrinkles will vanish immediately, or it may be delayed, in which case it will take time for the wrinkles to disappear (Cooke & Roth,. 1956).

A wrinkle resistant finish is applied to a textile in order to make the textile resistant to wrinkling and to assist the textile in a rapid recovery from wrinkling after it is worn. The effectiveness of the wrinkle-resistance finish depends upon the fiber content of the fabric, the construction of the fabric and the particular chemical formulation that is applied as the finish. This innovative fabric treatment works by strengthening the molecular bridges that connects cellulose molecules in a cotton fiber. The special process stabilizes the hydrogen bridges. This permits the fabric to retain its smooth surface, even after numerous washing. The finish does not alter cottons durability, colour clarity or natural absorbency (Logue & Hall, 1994).

Crease resistant finishes typically cause the textile to become stiffer, less absorbent, and more resistant to wrinkling. The strength and abrasion resistance of the textile is sometimes lowered, especially when the textile contains cellulose fibers. The extent of the durability of the finish depends upon the percentage of the resin retained in the textile (Logue & Hall, 1994).

2.2. DIRECT DYES.

Direct dyes are water soluble dyestuffs which are absorbed by cellulosic fibers, such as cotton, linen and rayon from an aqueous solution containing electrolytes. Chemically, nearly all Direct dyes are azo compounds containing sulphonic acid groups to impart aqueous solubility, the dyes themselves being the sodium salts of these aromatic sulphonic acids. In general, Direct dyes are high molecular weight compounds containing two, three or more azo groups, although a few monoazo products are known. The remaining chemical classes are derived from stilbene, copper thalocynine, dioxazine, quinoline or thiazole structures (Nkeonye, 1987).

2.2.1. PROPERTIES OF DIRECT DYES.

Some of the properties of Direct dyes are;

They are water soluble anionic dyes.

When dyed from aqueous solution in the presence of electrolyte, are substantive i.e. have high affinity for cellulosic fibers. They also have poor fastness property (Sharma, 2011).

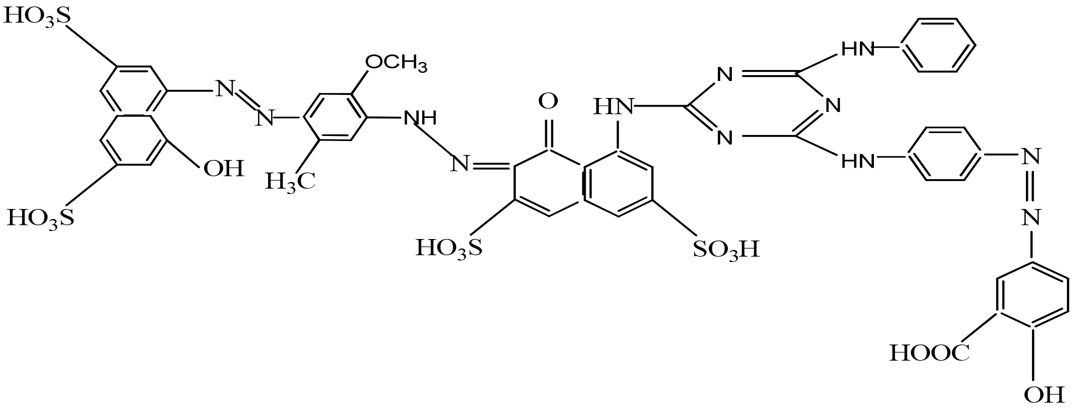
2.2.2. IMPORTANCE OF DIRECT DYES

Direct dyes are used in many applications both textile and non-textile field. In textile field is used in dyeing cotton, rayon, acrylics among others, while in the non-textile field, is used particularly for dyeing paper and leather (Nkeonye, 1987).

2.2.3. COMPOSITION OF DIRECT DYES.

The Direct dye classification in the colour index system refers to various planar, highly conjugated molecular structures that also contain one or more anionic sulphonate groups. It is because of this sulphonate groups that the molecules are soluble in water.

The introduction of the first substantive or direct dye for cellulose in 1884 aroused much interest, which led to extensive research and experimentation in attempt to uncover the structural characteristics which account for the very strong substantivity which many Direct dyes have for cellulose. The earliest theories offered purely mechanical explanation, attributing dye retention by the cellulose to its pore structure (Nkeonye, 1987). The structure below is an example of Direct dyes;



Structure 1: C.I Direct Green 26

2.2.4. APPLICATION OF DIRECT DYES.

The rate at which this dye is absorbed by the fiber and the amount that has been absorbed when the dyeing operation is complete are determined not only by the intrinsic substantivity of the dye for the fiber but also by the amount of salt used, the liquor ratio of the bath and its temperature. Adding salt to the bath improves the exhaustion. So also does an increase in the concentration of dye in the bath; this means that exhaustion, i.e. uptake of dye by the fiber, can be improved without the use of additional dye, simply by using less water in the bath, i.e. by reducing the liquor ratio. This may not always be possible, however, because the use of low liquor ratios may cause operational difficulties. An increase in temperature increases the rate at which the dye is taken up and also the rate at which it migrates or levels when on the fiber; however, it is important to note that rise in temperature also reduces the equilibrium exhaustion (Charles, 1974).

2.2.5. FASTNESS PROPERTY OF DIRECT DYES.

The main set back of Direct dyes is their rather low fastness to wet treatments and sometimes also to light. Their washing fastness may be described as poor to moderate, while their fastness to light varies from poor to very good. Fastness to washing and light is improved, in suitable cases, by subjecting the dyed fabric to an after-treatment.

2.2.6. DEVELOPMENT OF DIRECT DYES.

It has often been pointed out that the event which initiated the period of major growth and establishment of the synthetic dye industry was the discovery in 1884 of congo red, the first direct dye for cotton, rather than the more romantic story of perkins pioneering efforts thirty years earlier. Direct seem to have lingered in the shadows, hovering at the unfasionable end of comparisons with the ultra-durable vats or the ultra-bright reactives. Even recent pronouncements in the media implying that azo dyes in general could be carcinogenic, rather than the very few members of the class, actually demonstrated to be so in animal tests, seem likely to tarnish the image of Direct dyes disproportionately. At least 70% of all Direct dyes are un metallised azo compounds and it must be admitted that congo red was synthesized from benzidine, now universally recognised to be carcinogen.

Apart from efforts in recent years to find replacements for the benzidine-derived products that have been phased out, developments in the chemistry of Direct dyes have been few, compared with the much more active field of research on novel reactive systems. Never the less, Direct dyes have shown themselves surprisingly resilient in terms of their technical and commercial importance. They have represented about 20-30% of the total U K production of dyes for cellulosic textiles for at least sixty years and have remained as important to dyers in many overseas countries.

The primary reason for this is probably due to the essential simplicity of the dyeing process, but a separate after-treatment to enhance wet fastness has been a feature of most direct dyeing since the end of the last century. Development taking place during the most recent decades, however, have reached new levels of sophistication and enabled Direct dyes to amount a counter-attack against Reactive dyes in the battle ground of severe wet fastness requirements (Shore 2008).

2.2.7. AFTER TREATMENTS OF COTTON DYED WITH DIRECT DYE.

The generally poor wet fastness of Direct dyes is a great technical defect, particularly when used with materials which are likely to be subjected to repeated washing. As such various methods have been used to improve the fastness properties. Treatments by diazotization and coupling with metallic salts, with formaldehyde, with cationic fixing agent have been reported to be used (Nkeonye, 1987).

2.3. VINYL POLYMERS.

Vinyl polymers are polymers produced as a result of vinylation. Vinylation is a term used to describe the reaction between ethylene and compounds, such as alcohols carboxylic acids and amines which contain active hydrogen atom. (Uppal & Bhatia, 2006). Examples of vinyl polymers are; poly (vinyl alcohol), poly (vinyl butyral), poly (vinyl acetate), etc.

2.3.1. POLY VINYL ALCOHOL (PVA).

Poly (vinyl alcohol) was first prepared by Hermann & Haehnel in 1924 by hydrolyzing poly (vinyl acetate) in ethanol with potassium hydroxide. Poly (vinyl alcohol) is produced commercially from poly (vinyl acetate), usually by contentious process. The acetate groups are hydrolyzed by ester interchange with methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide. The physical characteristics and its specific functional uses depend on the degree of polymerization and degree of hydrolysis. Polyvinyl alcohol can be classified into two classes namely; partially hydrolyzed poly (vinyl alcohol) and fully hydrolyzed poly (vinyl alcohol) (Saxena, 2004).

2.3.1.1. PROPERTIES OF PVA.

Poly (vinyl alcohol) is an odourless and tasteless, translucent, white or cream coloured granular powder. It has excellent film forming, emulsifying and adhesive properties. It is also resistant to oil, grease and solvent. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However, these properties are dependent on humidity (Shakhashiri, 1989).

2.3.1.2. IMPORTANCE OF PVA.

Poly (vinyl alcohol) is used in various applications based on the degree of polymerization and degree of hydrolysis. It is used as an emulsion stabilizer, in textile warp sizes, as a moisture barrier, as an adhesive and thickener material in latex paints, paper coating, hairspray, shampoos, and glues. It is also used in protective chemical-resistant gloves, as a fixative for specimen collection, as a water-soluble film useful for packaging and so on (Saxena, 2004).

2.3.1.3. APPLICATION OF POLY (VINYL ALCOHOL) IN THE FINISHING OF FABRICS.

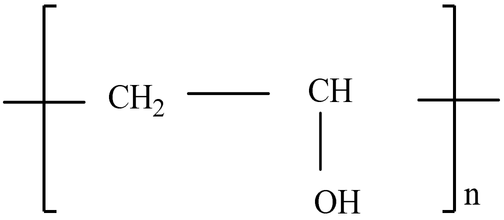
Prichard (1969) reported in his book polymer monograph the use of a thin coating of poly (vinyl alcohol) frequently used as a finisher to improve the feel or hand of textile fibers like cellulose acetate rayon when they are finally woven into fabric. The cross-section of fibers, when they are first formed, are far from uniform, and their surfaces possess degrees of roughness characteristic of the fiber and its formative process. In order to produce a smoother surface, the fibers are therefore coated. Pritchard further stated that a finish coating of poly (vinyl alcohol) is very suitable because it is smooth to the touch elastic and does not easily crack away from highly extendable yarn.

Finch (1973) reported that poly (vinyl alcohol) alone is not suitable for permanent finishing because of its water solubility, but can contribute to a number of advantages when added to other systems. The use of thermosetting resins of urea-formaldehyde, melamine formaldehyde and ethylene urea-formaldehyde types on cellulose fabrics has results in a great improvement in their recovery from wrinkling. Treatments with this thermosetting resins mentioned, contributes wrinkle and shrinkage resistance to fabrics. Depending on the type and take-up of the resin, however, the tear and bending resistance of the fabric may be lessened.

Edward & Czerwin (1966) reported the use of urea-formaldehyde and melamine-formaldehyde as resins that can be used as finishes for wrinkle and shrinks resistance. However, the bending resistance of the fabric is lessened unless a modifier is used, e.g. poly (vinyl alcohol).

2.3.1. STRUCTURE OF PVA.

Poly (vinyl alcohol) is produced as a result of hydrolysis of poly (vinyl acetate), it is a polymer with a repeating vinyl alcohol unit and its molecular weight can range from 25,000 to 300,000 (Shakhashiri, 1989).



$$\left[- CH_2 - \underset{OH}{\underset{|}{CH}} - \right]_n$$

Structure 2; PVA

2.3.2. POLY (VINYL BUTYRAL) (PVB).

Poly (vinyl butyra1) (or PVB) is a resin usually used for applications that require strong binding, optical clarity, adhesion to many surfaces, toughness and flexibility. It is prepared from poly (vinyl alcohol) by reaction with butyraldehyde. The major application is laminated safety glass for automobile windshield (Manfred *et al*, 2000).

2.3.2.1. PROPERTIES OF POLY (VINYL BUTYRAL).

Poly (vinyl butyral) resins have a combination of properties that make them a key ingredient in a variety of successful formulations. Some of these properties for which poly (vinyl butyral) is widely used are outstanding binding efficiency, optical clarity, adhesion to a large number of surfaces, and toughness combined with flexibility (Manfred *et al*, 2000).

2.3.2.2. IMPORTANCE OF PVB.

Poly (vinyl butyral) is very important due to its wider application in various fields, such as in textile coating, wood coatings, ceramic binding inks and dry toners etc.

Poly (vinyl butyral) resins are employed in a wide array of industrial and commercial applications. These unique resins offer impressive performance, as well as outstanding versatility. (Mathew, 1997).

2.3.2.3. APPLLICATION OF POLY (VINYL BUTYRAL).

Some of the applications in which PVB is a vital ingredient include:

Ceramic binders, inks/dry toners, wood coatings, wash primers, composite fiber binders, structural adhesives and other diverse uses.

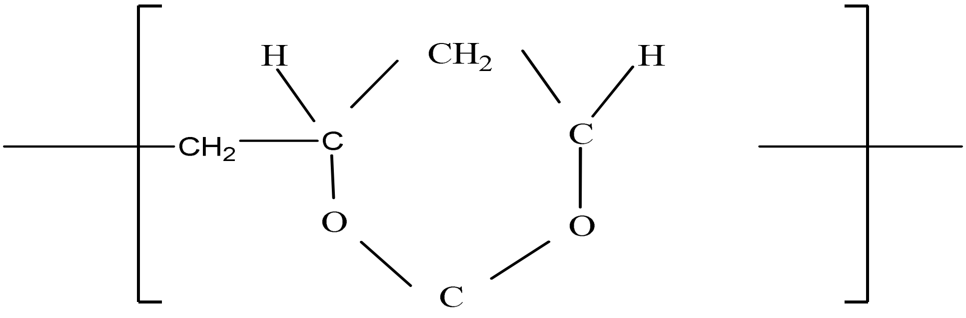
PVB resin was pioneered by Monsanto in the 1930s as the key ingredient for automotive safety glass inter layers. It still enjoys widespread use in automotive and architectural applications for laminated safety glass (Manfred *et al*, 2000).

2.3.2.4. STRUCTURE OF POLY (VINYL BUTYRAL).

Acetals, such as poly (vinyl butyral), are formed by the well-known reaction between aldehydes and alcohols. The addition of one molecule of an alcohol to one molecule of an aldehyde produces a hemiacetal. Hemiacetals are rarely isolated because of their inherent instability but, rather, are further reacted with another molecule of alcohol to form a stable acetal.

Poly vinyl acetals are prepared from aldehydes and poly (vinyl alcohols). Poly (vinyl alcohols) are high molecular weight resins containing various percentages of hydroxyl and acetate groups produced by hydrolysis of poly (vinyl acetate).

The conditions of the acetal reaction and the concentration of the particular aldehyde and poly (vinyl alcohol) used are closely controlled to form polymers containing predetermined proportions of hydroxyl, acetate, and acetal groups. The final product may be represented by the following stylized structure.



Structure 3; PVB

2.3.2.5. ADVANTAGES OF PVB AS FABRICS FINISH.

The advantages of PVB as a textile coating resin stem from the following properties:

- Transparency: PVB can be made into a clear, colourless coating with excellent light resistance and aging characteristics.

- Adhesion: After curing, PVB adheres readily to practically all fabrics, including those normally considered difficult to coat, such as nylon, viscose rayon, and fiber glass.

- Hand and appearance: A coating with PVB has the soft, warm, flexible feel of an uncoated fabric, yet possesses all the functional characteristics of coated fabrics.

- Functional properties: PVB combines these attributes with functional properties comparable to those of the best textile coating materials in the field. During the drying and curing operations, PVB is transformed to an elastomer which becomes a permanent part of the fabric.

Fabrics coated with properly compounded and cured PVB have outstanding softness and flexibility without tackiness of low softening temperatures. They have excellent chemical and water resistance. Films of PVB resin are tough and will resist abrasion and wear. Coatings can be applied from high solids solutions made with common solvents. (Mathew, 1997).

CHAPTER THREE

3.0. MATERIALS AND METHODS

3.1. MATERIALS.

The instruments used were; FTIR (carry 630 FTIR), light fastness tester (Microscal), crease recovery tester, universal tester (Model: WDS-3), abrasion resistance tester (Model No: 103-1386-2).grey scale for assessing change in colour (ISO 105 A02, BS1006 A02 1978),

3.2. PREPARATION PROCESSES

3.2.1. PRE-TREATMENT OF THE COTTON FABRICS.

A grey fabric needs to be subjected to a preparatory process before dyeing otherwise very poor colour yield will result. These process includes, scouring mercerisation and bleaching.

3.2.1.1. SCOURING.

The object of scouring is to remove impurities such as wax (or fat), protein and ash to a level low enough to permit dyeing.

Hot alkaline solution (caustic soda) was used on cotton. Scouring was accomplished by boiling the material in a bath containing 4% caustic soda for 45 mins, followed by thorough washing in water and drying. (Nkeonye, 2009).

3.2.1.2. MERCERISATION.

Mercerisation is a process originated by John Mercer in 1884, and it involves the treatment of cotton fabric in a concentrated solution of caustic soda (typically 25%)

for about 60 seconds at 20^0C. The material was then thoroughly washed in water and rinsed to remove the alkali, and dried. (Nkeonye, 2009).

3.2.1.3. BLEACHING.

Bleaching was carried out in order to destroy the natural colouring matter. Hydrogen peroxide is a more common bleaching agent for cotton. It bleaches under alkaline condition. (Nkeonye, 2009).

Two solutions of 20% H_2O_2 and 10% $MgSO_4$ was mixed and 200ml of water was added. The cotton fabric was immersed inside the solution and the mixture was heated in a beaker which boils for 30 minutes. The cotton fabrics was removed, washed with distilled water and dried at room temperature.

3.2.2. PRODUCTION OF CROSS-LINKED POLY (VINYL ALCOHOL) AND POLY (VINYL BUTYRAL)

The cross linked PVA was synthesized using similar procedure reported by (Busuguma, 2010)

A solution of 24g (0.000192mol) of PVA in 576g of water was prepared and heated to 60^0C. 2ml of 25% solution of Urea was added and the solution was stirred for 30mins. While stirring continued 15ml of 0.1M HCl was added. After one hour stirring, 50ml of 0.1M NaOH was added.

The same procedure was used for cross-linking PVB.

3.3. DYEING COTTON FABRIC WITH DIRECT DYES.

The method of dyeing adopted was the method cited by Nkeonye (2009).

0.2g of the dye (Direct yellow H.E.6G) was dissolved in 400ml of water. 2.0g of common salt (NaCl) was added. 20g of well prepared fabric was entered into the dye bath and raised slowly to the boil, the material was stirred to get an even dyeing. The dyeing continued at this temperature for 40 minutes, then removed from the dye bath rinsed in cold water, squeezed and dried.

The same procedure was adopted for Direct brown.

3.4. APPLICATION OF CROSS-LINKED PVA AND PVB TO COTTON FABRICS.

The method adopted was the one reported by Logue & Hall (1994) and Nkeonye (1987).

A cut sample (20cm by 15cm) was coated with the cross-linked polymer (PVA/Urea) and allowed to air dried. It was later damped and allowed to condition for 2 hours, then calendared using a conventional pressing stone.

The same procedure was adopted for PVB/UREA cross-linked polymer.

3.5. CHARACTERIZATION.

3.5.1. FTIR SPECTROSCOPY.

The infra-red spectra of the samples were obtained using the polymer samples directly. The model of the machine used for the analysis is Carry 630 FTIR. All the spectra were recorded over the range of 4000-650cm^{-1}. As a preliminary survey of the spectra has shown that, all the reliable structural data are covered in this region.

3.5.2. DETERMINATION OF DENSITY.

The densities of the polymers were determined using density bottle. To calculate density of each sample, the following relation was used;

Density of the sample=weight of the sample/volume of the sample.

3.6. ANALYSES OF TREATED COTTON FABRICS.

The dyed cotton fabrics both treated and untreated were subjected into various analyses which includes,

3.6.1. FASTNESS PROPERTIES.

An aspect of fabric which is always of interest is its colour. Some dyes may be fast to washing and dry-cleaning but not to day light. Others may be fast to perspiration and rubbing when wet, but not to hot pressing, bleaching and so on. As such the fabrics treated were subjected to the following fastness tests which are of particular interest to the fabric.

3.6.1.1. FASTNESS TO WASHING.

This method is intended for determining the resistance of the colour of textiles in all forms to the repeated action of soap solution as used in washing (Nigerian Industrial Standard, 1973).

5g of an appropriate soap was dissolved in a litre of distilled water (soap solution). The specimen was placed in a 250ml beaker, 50ml of the soap solution prepared was added to 1g of the sample which give a liquor ratio of 50:1. The specimen was then heated at 48^0C using a regulated water bath for 45mins. Finally, the specimen were rinsed twice in cold distilled water and then in cold running water for 10mins then it was squeezed and dried.

The dried specimens were assessed using the standard grey scale for assessing colour change.

3.6.1.2. FASTNESS TO LIGHT.

All the samples were cut into an appropriate size and were exposed alongside with the standard dyed blue wool fabrics to the artificial light for 96 hours. (Burkinshaw & Kumar, 2009).

3.6.2. PHYSICAL TEST OF THE TREATED FABRICS.

Generally, for every type of finish employed to a fabric it must be accompanied by various physical tests to determine the change in properties of the treated fabric in relation to the untreated one. Below are some of the physical tests employed to all the samples.

3.6.2.1. FEEL TO HAND TEST.

The treated and the untreated samples were touched with hand and the smoothness of the fabrics was assessed by the feel of the hand. (Pritchard, 1969).

3.6.2.2. TENSILE STRENGTH TEST.

All the treated and the untreated samples were tested for their tensile strength using the universal tester (Model: WDS-3), which constitutes of an upper and a lower jaw that were used to grip (hold) the samples. As the machine is switched on, the upper jaw moves upward to exert force or load on the sample, the machine stops automatically as the sample breaks or ruptures. The length at which it extended before break and the force applied (in Newton) is recorded. It is found that the gauge length of the machine is 40mm.

3.6.2.3. WEAR AND ABRASION RESISTANCE TEST.

The aim is to determine the resistance of textile fabrics to abrasive actions.

Wear is the net result of a number of agencies which can reduce the severe ability of the fabrics. Abrasion resistance is one aspect of wear which can give an indication of wearing properties.

The specimens both treated and untreated were tested for wear and abrasion resistance using abrasion resistance tester (Model No: 103-1386-2), the samples were cut or punched into a flat or circular shapes of 38mm diameter, and were further mounted in a specimen holder with circular piece of foam of 38mm diameter behind each. The abradant was tensioned by placing a weight on the surface of the abradant before tightening up the retaining frame. The machine continues abrading the specimens until two threads were broken. The time and the number of rubbing that force it to break were recorded.

3.6.2.4. CREASE RECOVERY TEST.

The property and the bending characteristics of material give information about the material. That is how easy it is for the material to recover from deformation. Therefore, crease recovery of a fabric is a measure of the ability to recover from folds, and creases that would otherwise distort the aesthetics appearance of the fabric.

All the treated and untreated samples were tested for crease recovery angle using a crease recovery testing machine, the materials were cut in pieces both in warp and weft direction. The measurement was 5cm long and 2.5cm wide. Crease displacement was obtained by folding the specimen half and placing it between a glass plate and adding 2kg weight to it.

The specimen was then creased for 1min and transferred to the fabric clamp on the instrument. It was then allowed to recover for about a minute. The die of the instrument was then rotate to keep the free edge of the specimen in line with the knife edge in order to determine the crease recovery angle.

CHAPTER FOUR

4.0. RESULTS AND DISCUSSION.

4.1. RESULTS OF PRE TREATMENT OF THE COTTON FABRICS.

4.1.1. SCOURING.

During the boiling process, the oils and fats on the textile became converted to soaps by the caustic soda, and this soap emulsifies the waxes. The emulsified waxes and other solubilised impurities are removed during washing and rinsing in water. (Nkeonye, 2009).

4.1.2. MERCERISATION.

At the end of this treatment, the process significantly increased the dye affinity of the fibre relative to that of an untreated material. (Nkeonye, 2009).

4.1.3. BLEACHING.

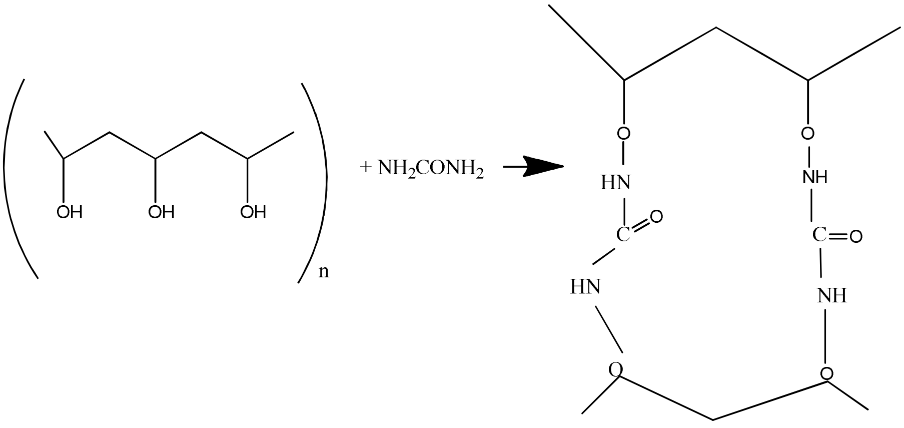
The bleaching process destroys the natural colouring matter in the cotton by oxidation. (Nkeonye, 2009).

4.2. FORMATION OF CROSS LINKED POLY (VINYL ALCOHOL) AND POLY (VINYL BUTYRAL).

The cross linking of poly vinyl alcohol/urea yielded the formation of micro gels structure resulting from the action of the cross linking agents on a diluted solution of PVA, also, the cross linking of PVB/Urea gave a less viscous solution resulting from the action of the cross linking agents.

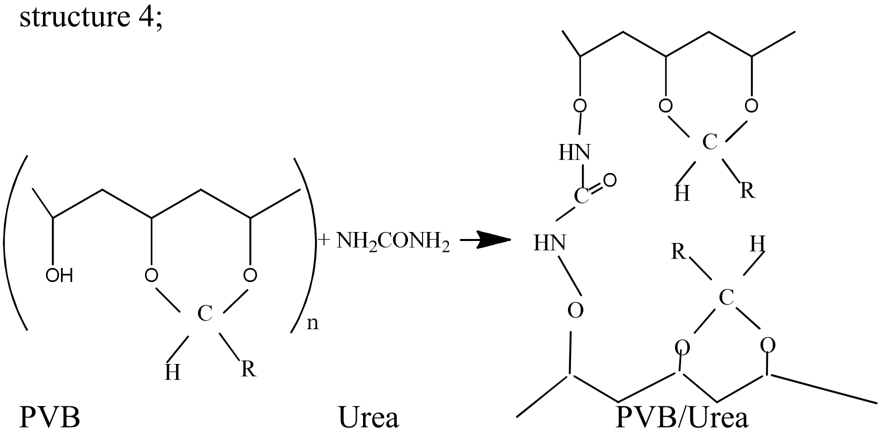
4.2.1. PROPOSED STRUCTURE OF THE CROSS-LINKED PVA AND PVB

The hydrogels synthesized in this research was the PVA-Urea hydrogels formed as a result of cross linking poly (vinyl alcohol) with Urea and PVB-Urea as a result of cross-linking poly (vinyl butyral) with urea. A reaction was shown below to show the cross-linking reaction.



PVA Urea PVA/Urea

structure 4;



PVB Urea PVB/Urea

Structure 5;

4.4. RESULTS OF THE CHARACTERIZATIONOF CONVENTIONAL AND CROSS-LINKED PVA AND PVB.

4.4.1. FTIR SPECTRA FREQUENCIES OF THE POLYMERS.

The FTIR spectra frequencies of the polymers were summarized in Table 1

TABLE 1 FTIR spectra frequencies.

Group	CPVA	PVA/UREA	CPVB	PVB/UREA
O-H	3280cm^{-1}			
C-O	1091 cm^{-1}	1095 cm^{-1}	1000cm^{-1}	1048 cm^{-1}
N-O		1330 cm^{-1}		1382 cm^{-1}
C-H	2907cm^{-1}	2944cm^{-1}	2937cm^{-1}	

From the typical spectra on Table 1 for the conventional PVA, the band at 920.91 cm^{-1} is related to the syndiotactic structure of the polymer, strong O-H stretching at 3280 cm^{-1} is related to strong O-H bands for free alcohols. An important peak at 1091 cm^{-1}is assigned to C-C and C-O stretching, which is an assessment tool of PVA structure because it is a semi crystalline synthetic polymer. In the PVA, There is also a strong C-H alkyl stretching at 2907 cm^{-1}.

By cross linking PVA with Urea, the O-H stretching at 3280 cm^{-1} was removed and N-O bond was established at 1330cm^{-1}. The C-O and C-C band was shifted to 1095cm^{-1}, likewise, the C-H band was shifted to 2944cm^{-1}.

In the PVB spectra, a band at 1000cm^{-1} was observed which indicated the presence of C-C and C-O bond. There is also a strong C-H alkyl stretching at 2937cm^{-1}

After cross linking PVB with urea, a band at 1382 cm^{-1} is established indicating that there is a N-O bond, The C-C and C-O band was shifted to 1048cm^{-1}.

4.4.2. DENSITY OF THE POLYMER.

The densities of poly (vinyl alcohol) and poly (vinyl butyral) in relation to the cross linked ones are shown in Table 2

Table 2; Densities of the conventional and cross-linked polymers.

Sample	Density(g/cm^3)
CPVA	0.99025
PVA/Urea	0.9955
CPVB	0.817
PBV/Urea	0.824

From the results above, it is clearly seen that the density of cross-linked PVA (PVA/Urea) is higher than that of the conventional PVA. This is due to the fact that the formation of micro-gels left the solution with more water than that of the conventional.

Likewise, the density of cross-linked PVB (PVB/Urea) is higher than that of the conventional PVB, this is due to the fact that, CPVB/Urea contains more water than the conventional one (James 2008).

4.5. RESULTS FOR DYEING OF COTTON FABRICS AND AFTER TREATMENT.

Both cotton fabrics dyed with direct dyes (direct brown and yellow HE 6G) gave medium shade levelled very well. The after-treatment improves the fastness properties of the colour of the dyed fabrics as well as the mechanical properties.

4.6. ANALYSES OF TREATED COTTON FABRICS.

The results of various analyses obtained were summarized below.

4.6.1. FASTNESS PROPERTIES.

4.6.1.1. FASTNESS TO WASHING.

To qualify for the label ''fast to washing'' a minimum rating of 3 in the scale 1-5 is required for the change in colour. Below are the results obtained from the visual assessment of change in colour using the grey scale that includes half steps.

Table 3; Washing fastness results of the treated and untreated fabrics.

Specimens	Fastness
FAA	2
FAB	4
FAC	3
FBA	2
FBB	4
FBC	3

From the result above, it is seen that, those fabrics treated with PVA/Urea exhibited better washing fastness than those treated with PVB/Urea, this could be due to the partial solubility of PVB in water, however, show good fastness to washing than the untreated ones.

The washing fastness could possibly be due to the formation of large molecular size, low water solubility thin gels situated at the surface of the dyed substrate which physically resisted diffusion of the dye from dyed fabric during washing (Burkinshaw & Kumar, 2009).

4.6.1.2. LIGHT FASTNESS.

For a sample to qualify for the label ‘fast to light’ a minimum rating of 5 in the scale 1-8 is required. Below are the results obtained from the light fastness test of the specimens.

Table 4 Light fastness results of both treated and untreated fabrics.

Specimens	Fastness
FAA	3
FAB	6
FAC	7
FBA	3
FBB	6
FBC	7

The treated samples generally showed good light fastness more especially those treated with PVB/Urea, which showed moderate washing fastness. This was possibly because the direct dyes used exhibited good fastness to light, and also there are some cases where improvements in particular fastness properties obtained at the expense of another fastness (Nkeonye, 1987).

4.6.2. RESULTS FOR THE PHYSICAL TEST PROCESSES.

4.6.2.1. RESULTS FOR THE FEEL TO HAND.

It is observed that the smoothness of the samples treated with PVA/Urea and PVB/Urea were much better improved when compared with untreated one. The smoothness (feel to hand) could be due to the smooth to touch, elastic property of thin film of poly (vinyl alcohol) and poly (vinyl butyral) when coated on a fabric (Prichard, 1969 & Mathew, 1997).

4.6.2.2. TENSILE STRENGTH RESULTS.

TABLE 5; Tensile strength results of both treated and untreated fabrics. (warp yarn)

Tensile strength for warp specimens

Specimens	Force applied (N/tex)	% elongation/extension (mm)
FAA	80.2530	10.4120
FAB	122.8210	7.1241
FAC	126.4561	7.9863
FBA	90.6272	9.6510
FBB	129.4160	5.2481
FBC	134.5431	8.5162

TABLE6; Tensile strength results for both treated and untreated fabrics (weft yarn).

Specimen	Force applied (N/tex)	% elongation/extension (mm)
FAA	86.4392	12.3291

FAB	109.7210	12.4540
FAC	117.5471	11.3210
FBA	101.6071	13.6200
FBB	115.7620	8.7798
FBC	141.6410	10.3721

From the results of tensile strength of both treated and untreated samples, it can be seen that the treated dyed samples have higher tensile strength than the untreated ones. This was possibly due to the higher force needed for the rupturing of the treated samples than that of the untreated, which is in line with the fact that tensile strengths of materials are defined as the resistance of materials to tensile forces that tend to pull it apart. (Redmond, 2007).

4.6.2.3. RESULTS FOR WEAR AND ABRASION TEST.

Wear and abrasion resistance test is carried out to measure the time it will take for the fabric to wear. The results of the time (min) and number of rubbing of the various specimens are shown below;

TABLE 7; wear and abrasion resistance results

Specimens	Time (min)	no of rubs
FAA	2:30	124
FAB	4:30	170
FAC	13:42	300
FBA	0:45	55
FBB	4:33	141

FBC	10:00	266

The results above showed that the treatment given have greatly improved the wear and abrasion resistance of the fabrics. On the other hand, those fabrics treated with poly (vinyl butyral) exhibited better performance in terms of wear and abrasion resistance than those treated with poly (vinyl alcohol). This is due to the facts that films of PVB resin are tough and will resist abrasion and wear. (Mathew 1997)

This has also shown that the treatment has imparted resistance mechanically to the fabric, which is contrary to other finishes that sometimes reduce the strength and abrasion resistance of fabrics (Logue & Hall, 1994).

4.6.2.4. RESULTS FOR THE CREASE RESISTANCE.

The crease recovery angles taken by the specimens from face and back for both warp and weft are summarized below;

Table 8; Results for the crease resistance of both treated and untreated fabrics.

Specimens	Angle of recovery (warp)		Angle of recovery (weft)	
	Face	back	Face	back
FAA	88.7	87.6	80.1	91.8
FAB	118.2	123.6	112	111.6
FAC	103.8	102.8	102.6	112.2
FBA	84.1	88.3	79.5	83.9
FBB	128.8	109.8	109.4	114.8
FBC	124.2	121.6	119.6	112.6

The results of the crease recovery of the fabrics have shown clearly the increase in angle of recovery of the samples that were treated to be higher than the untreated samples. The results entails that higher the angle of recovery the better the crease resistance of the fabrics. Therefore, this has shown that all the treatments were able to impart crease and wrinkle resistance to the fabrics.

This was in line with the report in a US patent that stated that crease resistance finishes typically cause the textile to become stiffer, less absorbent and more resistant to wrinkling. The report further showed that the extent of the durability of the finish depends upon the percentage of the resin retained in the textile (US Patent 5320645, 1994).

CHAPTER FIVE

5.0. CONCLUSIONS AND RECOMMENDATIONS.

5.1. CONCLUSIONS.

In conclusion, both poly (vinyl alcohol) and poly (vinyl butyral) were cross-linked with urea and the densities of conventional and cross-linked polymers were determined, it was found that the densities of cross-linked polymers are higher than that of the conventional ones. The FTIR spectroscopy was also carried out for both cross-linked and conventional polymers and some changes were observed on the bands.

In terms of physical and mechanical properties like wear and abrasion resistance, crease/wrinkle resistance, tensile strength and fastness properties, it was found that the treated fabrics exhibited better performance than the untreated fabrics.

5.2. RECOMMENDATION.

This research focuses on the use of poly (vinyl alcohol) and poly (vinyl butyral) separately. I recommend that further studies could be carried out by blending the two polymers together in proportion so that best modified polymers could be produced that will perfectly suit all the requirements for a wrinkle and crease resistance finish, and also serve as an after-treatment for cotton dyed with direct dyes.

REFERENCES

ACS (2004) American Chemical Society, National Historic Chemical Landmark, The evolution of Durable Press and Flame Retardant Cotton. Washington, D. C.Retreaved jan.01,2015,fromhttp://acswebcontent.acs.org/landmark/index.html

Berkley, E. E. (1942) Shrinkage and Cell Wall Structure of Cotton Fibers. American Journal of Botany, Vol. 29, No. 5, Pp. 416-423.

Burkinshaw, S.M. and Kumar, N. (2009).Poly(Vinyl Alcohol) as an After treatment: Part 3 Direct Dyes On Cotton. University of Leeds, Leeds LS29JT, U.K. Abstract retrieved Feb. 2015.

Busuguma U. A., (2010). Study on the Use of Cross-linked Poly (Vinyl Alcohol) as a Finish and an After treatment of Direct Dyes on Cotton Fabrics. An MSc Research, Department of Pure and Industrial Chemistry, Bayero University Kano.

Charles, H. G. (1974). A Laboratory Course in Dyeing.Third edition, pp. 65-67.

Cooke, T. F. And Roth, P. B. (1956).Finishing of synthetic fabrics. Textile Resin Department, American Cynamid Company, Bound Brook, New Jersey, p. 229.

Edward D and Czerwin, P. (1996). Modern Textiles Magazine, December 29.

Fernandez, M. D., Fernandez, M. J. And Hoces P. (2006). Synthesis of Poly(vinyl butyral) in homogenous phase and their Thermal Properties. Journal of Applied Science, Vol. 102, no. 5, 5007-5017.

Finch, C. A. (1973).Poly(vinyl alcohol) “Properties and Application”. Croda Polymers Ltd., Luton. John Wiley and sons L td.Pp 17-25, 214-220, 269-273, 391-410 and 556-559.

Georg L. Droke, Jr. & John D. Guthrie, (1959). Imparting Crease Resistance and Crease Retention to Cotton with APO. Textile Research Journal. Vol. 27, Pp 156-157. (2011).

Graves, L. R. (1997). Urea-formaldehyde Resin, Composition and Method there of. US Patent 5674971.

James, J. 2008. Percent solution, Viscosity and Density, Department of Energy Science Education, U S A. Retrieved march 2015, from http://www,sci.doe.gov.

Kamal, A. (1971). Crease Resistant Cloth From Partially Carboxymethylated Cotton Capable Of Reactive Dyeing. Textile Research Journal. Vol. 20, Pp255-256, (1970).

Kandolph S. J. (2007). Textiles (10th edition). Upper saddle, Nj: Prentice Hall. http://www.cotton ink.com/did you know. Retreived Sept. 19th ,20014.

Kandolph, S. J., Langford, Anna, L.,Hollen, N. And Jane, S (1993). Textile Macmillan New York, pp 1-2

Logue, B. T. And Hall, D.M. (1994). Process for imparting Wrinkle Resistance and Durable press finish to a fabric garment. US patent 5320645.

Manfred L. and Hallen L. (2000) ‘Po1yvinyl Compounds, Others” in Ullmann’sEncyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim.Doi: 10. 1002/14356007.a2 1743

Matthew D. Irving Synthesis and Characterization of Poly (vinyl butyral) Graft Copolymers. A Doctoral thesis.Lough BoroughUniversity. (1997)

Nigerian Industrial Standard 26: Standard methods for assessing fastness of coloured Textile.USD 677.01:535. 68:628.92.

Nkeonye, P. O. (1987). Fundamental Pinciples of Textile Dyeing. Printing and Finishing. Ahmadu Bello University Printing Press,Zaria pp57-70

Nkeonye, P. O.(2009) Introductory Textiles For Home Economists, Students of Arts and Beginners Generally. Ahmadu Bello University Printing Press,Zaria.

Olivera S. And Karinstana k. (2010). Differences Between Cotton and Viscose Fibers Cross-linked with BTCA.

Prichard, J. G. (1969). Poly(vinyl alcohol). Basic Properties and Uses. Polymer Monograph Vol. 4. Westham College of Technology, pp 1-7, 31-34 and 107-108.

Redmond, W. A; (2007). Microsoft Corporation, “Resins”, Microsoft students 2008 (DVD).

Reeves, W. A. (2007). Cotton Cross-linked at various degrees of swelling. Textile Research Journal, pp. 179-192.

Saara J. K. And Anna, L. L. (2009). Textile/8 ed. Prentice-Hall, Inc. Simon and Schuster/ A Viacom company Upper Saddle river, New jersey, 07458, pp.33-42.

Saxena, S. K. (2004). Poly (vinyl alcohol). Chemical and Technical Aassessment (CTA). Firt draft.

Shakhashiri, B. Z. (1989). Chemical Demonstration, University Of Wisconsin.Vol. 3, P.326.

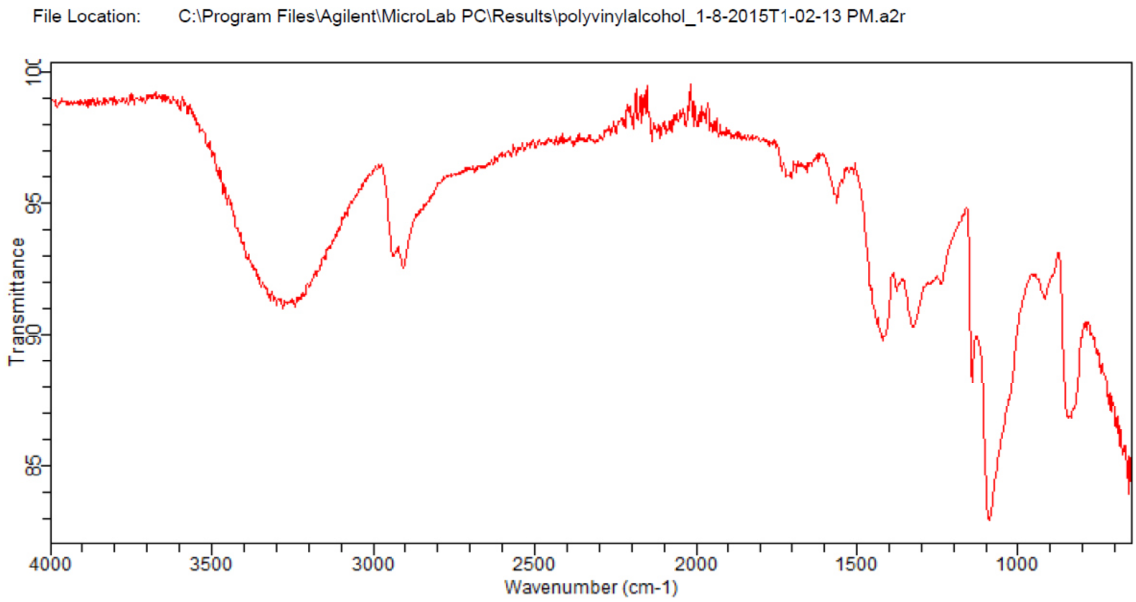
Sharma, B. K. (2011). Industrial Chemistry (including Chemical Engineering). Goel Publishing House, Krishna House, India, P 5.

Shore, J. (2008). Development In Direct Dyes For Cellulosic Materials. Online Library.Willy.com... Vol. 21.

Uppal, M. M. And Bhatia, S. C. (2006). Engineering Chemistry (Chemical Technology).

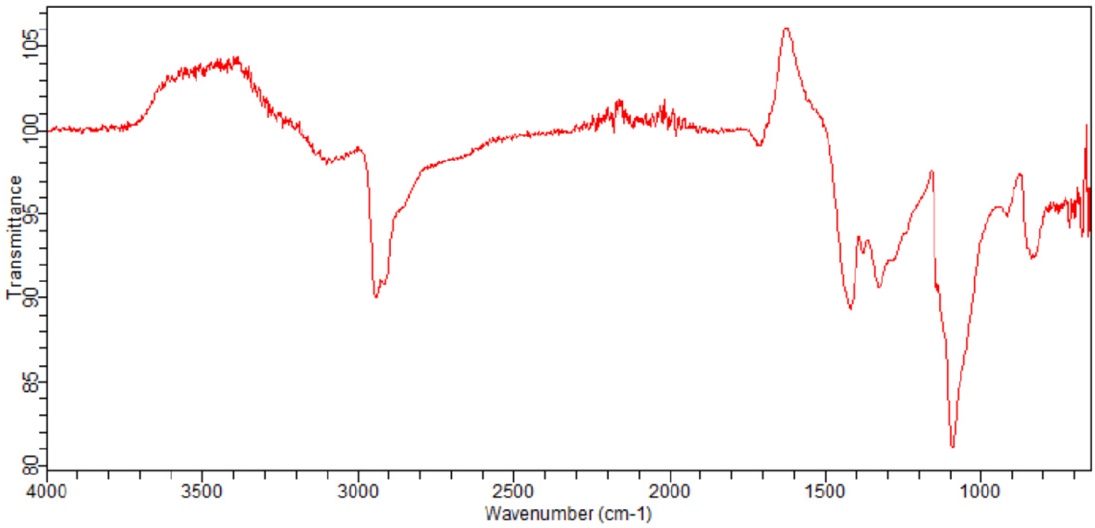
APPENDIX I

Conventional Poly (vinyl alcohol)



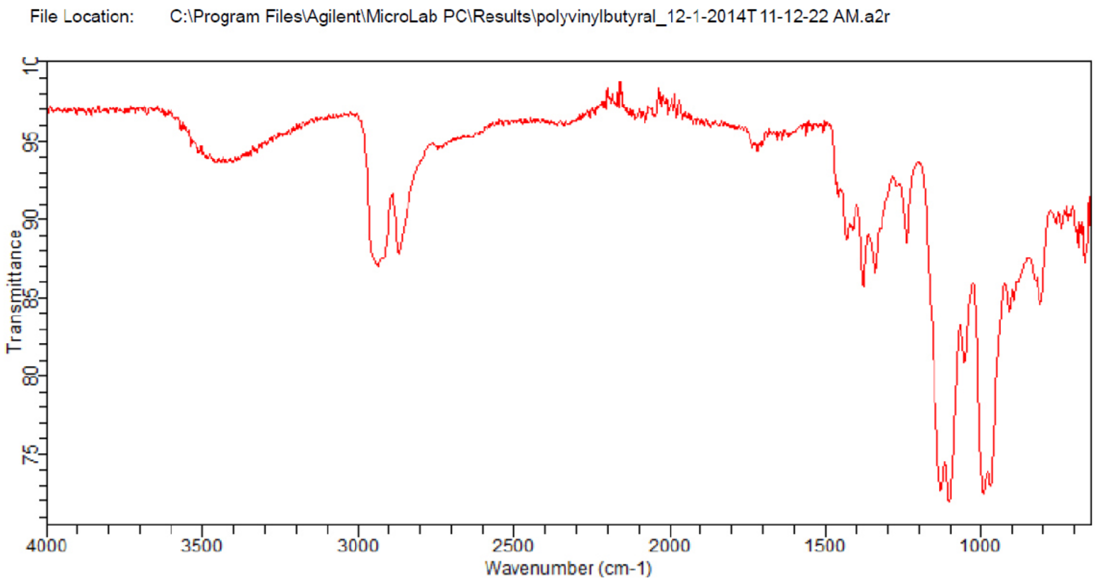
APPENDIX II

PVA cross-linked with Urea



APPENDIX III

Conventional poly (vinyl butyral)



APPENDIX IV

PVB Cross-linked with Urea