1.1 Introductions of denim dyeing

1.1.1 Background of Denim Fabric

Denim, as shown in figure 1.1, is a rugged cotton twill textile, in which the weft passes under two or more warp fibers. It produces the recognizable diagonal ribbing characteristic on the fabric, which distinguishes denim from cotton duck. It is a twill-weave woven fabric that uses different colours for the warp and weft. One colour mainly used on the fabric surface is indigo blue. This produces an effect of surface dyeing.

There are two types of denim fabric dyeing. They are indigo dyeing and sulphur dyeing. Indigo dyeing produces conventional blue colour and shade alike to blue colour. Sulphur dyeing, which also called colour denim is used to produce particular colours like black, cherry, grey, rust, mustard and lime, and also to get better the quality.

Both of them are vat dyestuff. They are insoluble in water and have a very poor affinity to cellulose fibers like cotton fiber. In normal situation, vat dyes will not attach on cotton fiber. For dyeing of cotton yarn, vat dyes should be transformed into water-soluble form via chemical reduction process, in which hydrogen is liberated. The hydrogen reacts with the dye and allows a water molecule to attach to the dye. The dye is then transported into cotton fiber by the media of water. Sodium hydrosulfite with sodium hydroxide is one of the reducing agents used to convert the dye to its soluble form. The dye is attached onto cotton fiber by the water. These reduced dyes have to then be oxidized. Oxygen reacts with the hydrogen to produce water. Removing the hydrogen makes the dye insoluble and results in the dye becoming physically trapped inside the fiber. (Ghoranneviss, M.)

In the past, denim has been famous in American custom since the late 18th century. “Denim” came from a French word “serge de Nimes”. Jeans are made from denim fabric and were originally made for labours. In the beginning, jeans were plain working trousers worn by labour. They became trendy among young groups in America in 1950s

Because of the popularity of denim products, especially denim jeans, they play as a vital role in fashion and textiles industry. Denim jeans present toughness and a slightly worn look for the fashionable appearance, which is the explanation why denim jeans are welcomed by various public around the world. The fade-out effect can be produced in nature or in manufacture process.

Dry denim means unwashed after being dyed. It is recognized to fade gradually as the customer wears the article made of denim. A number of consumers choose this type of denim for the reason that they can "age" their denim in a more natural way and can show their character. Manufacturer developed some unusual washing method on denim merchandises which can make a quick and standardized wash-out effect. It plays a very significant role on denim product development. These methods not only make denim more vintage and create more "high and low" effect in a short time, but also allow mass production for the development of denim market and give more choices for customers

1.1.2 Surface Dyeing Technology

Surface Dyeing means colours are only attached on the surface of the fabric or yarn instead of getting through to the core. The main benefit of surface dyeing is saving dyes and water. Some people look this as a dyeing defect and consider that dyes are not consistently distributed on the yarn. As a result, there is not much technology that can allow surface dyeing. On the other hand, there is a distinguishing feature of indigo dye called ring dyeing, where only an outer ring of fibers in the yarn is dyed and a white core is left.

Denim has one side in blue colour and the other side in white, giving an outcome of surface dyeing. However, the effect can also be produced by twill weaving. They use two different colours on warp yarn and weft yarn. Weaving structure makes one colour predominant on the fabric surface. Conventionally, blue denim is constructed in warp faced cotton fabric with 3 x 1 twill, where weft is left un-dyed and warp is dyed in a solid colour. In other words, it is one more type of surface dyeing as only one side of fabric is coloured. Part of the dyes and water are saved as only one yarn is dyed in the process.

Due to the feature of indigo dye, it can turn out a surface dyeing effect on the yarn. Only the surface of yarn is dyed and leaves the core in white. Normally, beam dyeing, sheet dyeing and rope dyeing methods are used for denim warp yarn. When abrasion occurred, indigo on the surface will be rubbed out and white colour will expose (Fig. 1.3). It results a fade out effect.

One more method of surface dyeing effect is foam dyeing. For foam technology, it uses air to substitute water as the transport media for the reaction agents. It is to lay the foam and dye on the fabric surface. Using foam technology as finishes for textile has great advantages over the traditional finishing techniques, such as reduction of the water usage during processes, energy saving in the drying of fabrics, reduction of chemical add-on, enhancement in the fabric physical properties, etc. Because of these benefits, it is more and more accepted in the textile industry, with a higher growth rate.

1.1.3 Wash out effect

The wash-out effect is achieved by removing dye particles of fabrics to get the popular abraded, worn out look during washing process. It is an aesthetic finishing by giving particular form of fabrics, especially denim. In this project, we aim at improving technology and suggesting an environmental friendly way for wash out effect so it is significant to know different denim washing methods in the market

They can be divided into two types: mechanical and chemical wash. The mechanical wash contains garment wash and stone wash. The chemical wash includes acid wash, enzyme wash and bleaching.

Garment Washing

Garment washing is a long-established washing method. It can provide fabrics a soft hand feel and natural clean visually. The denim is evenly singed and is scoured with a blend of phosphate esters before conducting open-width and rope washing to make sure that the denim will have pleasing softness and texture. Afterwards, it is washed with detergents at 60 - 90 ^{o}C for about 15 minutes in the industrial washing machines. At last, the fabric is softened and lubricated.

Stone washing

Stone washing provides a fading look for denim and increases the softness and flexibility. It is one of the traditional washing methods, but it has been improved by using other materials during the process. During the process, the newly dyed jeans are put in huge washing machines and are tumbled by pumice stones as abrasion (Fg.1.4). The stones have rough surfaces and remove some of the dye particles from the surface of the yarns to give jeans a worn-out effect.

Acid Washing

Acid washing is one of the traditional chemical washing method. It can give the garment a random, shaded look by washing out indigo dyes to create sharp contrasts in the colour and to reduce the stiffness of the denim. In this process, the dry denim cloth is bleached first. Pumice stones are pre-soaked in bleaching agents such as sodium hypochlorite or potassium permanganate. Then, the garments are tumbled in a rotating drum with the stones to remove the first colour layer of jeans chemically and mechanically for the fading effect. Finally, the garments are dried and the left hypochlorite is neutralized

Enzyme Washing

Enzyme washing is a relatively new technology on denim to achieve the worn appearance and to provide a soft handle for jeans since the enzyme cellulase removes surface fuzz. The process can be operated at low, warm or high temperatures. Denim is treated in enzyme baths in which organic enzymes loosen up the indigo dye and eat away cellulose fibers on the surface of the fabrics. When the jeans get the preferred colour, enzymatic reaction is stopped by altering the alkalinity of the bath. Special softeners and smoothing agents for softening cycles are utilized to give jeans a longer life

Bleaching washing

The bleaching effect is done by using an oxidative bleaching agent, e.g. sodium hypochlorite or potassium permanganate, with or without stone addition. The dark blue shade is decolourised by the bleaching chemicals, which destroy the indigo dye molecules. The bleached fabrics should be antichlored or washed with peroxide to minimize the yellowing and tendering of goods. The finished colour usually depends on the bleaching strength, liquor ratio and treatment time.

1.2 Problems of current methods

Surface dyeing allows the effect of colour fade-out which makes products more stylish and fashionable. However, there are some problems in current methods.

Denim fabric dyeing is limited to vat dyes only. As vat dyes are insoluble in water, the oxidizing process of vat is specially designed for vat dyes. For other dyes such as direct dyes, reactive dyes, and indirect dyes, they can dissolve in water. Then, we cannot prevent the dyes from getting inside the core of yarns.

There are needs to develop other dyes to replace vat dyes. This is because the particle of vat dyes is large; it will affect the hand feel of fabric. People accept that denim is stiff but if we further apply wash-out effect on other fashion products, we should not accept the stiff handle. Moreover, different type of dyes is suitable for different materials. If we develop more dyes for this finishing, it can be used in materials other than cotton.

For foam dyeing technology, it is difficult to control the absorbency and the shade of colour. Because different materials have variation in absorbency, variation in wet pick up ratio is resulted. Therefore, we need to try the application of chemicals for different fabrics which make the production not efficient. For some materials with low pick up ratio, we cannot get dark shade on the fabric because it cannot absorb enough dyes.

Some products and chemicals which are anti-foam formation cannot be used on the foam technology. For example, many commercial products including anti-foaming agents may forbid foam formation. Solvents and mineral oils also inhibit foam formation because they are used for certain processes that are not reacted with foam. Certain optical brightening agents, softeners and the existing of sulphate ions often reduce foam stability.

1.3 Objectives

There are several objectives of this study, including developing a simplified surface dyeing technology, achieving the wash-out effect on the cotton woven fabrics, environmental protection, developing more colourful fashion cotton and so on.

To begin with, the major objective of this research is to develop an agent that can simplify denim fabric dyeing process for producing colourful wash-out cotton fabric. As we know, the traditional wash-out effect for denim fabric is complicated. With the agent, we can develop a simplified process for surface dyeing and reaching the wash-out effect. Below figure 1.5 showed the concept of new wash out effect production.

The second objective is to find out the most suitable resin or materials that have the highest ability to form a molecular sieve polymer on the cotton yarn. At the same time, they can react with reactive dyes and allow the dyes stuff to stick on the sieve polymer surface.

Besides achieving the wash-out effect, we are aiming to develop an agent that will not affect the hand feel of cotton fabric and colourfulness. Normally, when the resins are cross-linked, it may become stiff in hand feel. Meanwhile, resins have reaction with the dyes that make colours become dull.

This study not only emphasizes on the achieving of fading effect on the fabrics, but also on the effects of fabrics which are required to meet the satisfactory application properties, such as rubbing colourfastness and washing colourfastness, for requirements of wash-out effect.

Moreover, this study focuses on protecting the environment. The application of surface dyeing agent can decrease the pick-up ratio of dyes, finally reducing the energy and water consumption. As the agent can produce a coating to avoid the dyes getting through the core of yarn, more fabrics can the dyed in the dye bath and, thus, the wastewater discharge reduces.

Last but not least, more colours for dyeing of the cotton woven fabrics are hoped to be developed, like cherry, yellow, ocean, navy and super black, etc., to cater for the customers' needs and to meet the fashion market.

1.4 Scope of Study

In this paper, the theory of forming a molecular sieve structure on cotton yarn will be studied. Pad-Dry Cure method will be used to cross link the molecule.

Three different materials will be tested to form a sieve structure on the cotton woven fabric. They are softener, DMDHEU resin and Knittex resin. The structure, the forming ability and the dyeing effect from reactive dyes of these materials will be evaluated.

Two different colours of reactive dyes will be tested on the sample in comparing the colour change and the colour fastness to washing and rubbing. Effect of colour fading by reactive dyes will also be evaluated.

2.1 General View of previous methods

As mentioned above, the traditional dyeing method of denim is to dye warp yarn separately before the weaving step. Therefore, denim manufacturing has unique preparation for warp yarn dyeing. On the other hand, filling yarn is put onto yarn packages and delivered directly to the weaving machine without any preparation before weaving (Wolf, Lauren 2011). The following flow chart (Fig. 2.1) shows the steps in manufacture of denim fabric and we will focus to talk about the dyeing part. From the chart, we can see that dyeing methods for denim warp yarn are rope dyeing, bean dyeing and slasher dyeing.

<u>Rope dyeing</u>

For rope dyeing, ball warps are continuously fed into the rope or chain-dyeing range for application of the indigo dyeing. The ropes are kept separated from each other throughout the various parts of the dye range. The ropes are first fed into one or more scouring baths, which consist of wetting agents detergents and caustic. It is to remove naturally occurring impurities found on the cotton fiber such as dirt, minerals, ash, pectin, and naturally occurring waxes. The purpose of this step is to guarantee uniform wetting and uniform dyeing. Then, ropes are fed into one or more water rinsing baths.

The next step is to feed rope into the indigo dye baths and skied after each dip. The ropes of yarn are rinsed in several water baths to remove any unfixed dye. If we want to have variation on the yarn colour, sulphur dye can be added. After the dyeing process, ropes will pass through squeeze rolls to extract water mechanically. The yarns are then dried and coiled into large tubs

<u>Slasher dyeing</u>

Slasher dyeing is a more convenient and reasonable method than rope method because rope dyeing using indigo is not desirable for manufacturers. The step of slasher dyeing is same as rope dyeing before the addition of dyes. For slasher dyeing, indigo is applied in a series of multiple dip and sky application to build up a fairly deep shades. If the arrangement of the slasher dyeing does not allow multiple dips and sky applications, then only light and medium shades can be obtained from indigo.

Slasher dyeing has a number of advantages and unique characteristics. Slasher dyeing employs a sheet of yarn, which is wounded directly onto a warp beam rather than ropes of yarn, so additional handling can be skipped. It can work well with lightweight denims. Moreover, this method requires less machines floor space, suitable for smaller production runs, so it has a quicker turn over time, and is more flexible in its response to changes in the market. This method required lower machinery cost and lower dye costs for specific fabric types. Additionally, the slasher dyeing technique can be used for other cotton dyes and thus can produce a wide variety of colours other than indigo blue.

Bean Dyeing

Bean dyeing is the most commonly used denim dyeing method. Most of the dyes are applicable for this method. They are sulphur dyes, reactive dyes, direct dyes, vat dyes as well as indigo. Therefore, it can provide large range of colour for denim fabric other than just indigo blue. Other than this advantage, bean dyeing can also be applied on both fabric and yarn in open width rolled onto a perforated beam. Further discussion on bean dyeing is in the below.

2.2 Beam dyeing technology

2.2.1 The background of Beam dyeing

One of the dyeing techniques that have been used for dyeing warp yarn for denim is beam dyeing. This techniques use not only indigo, but also reactive dyes, direct dyes as well as sulphur dyes and vat dyes so that it can provide a large range of colours to denim fabric. Therefore, this technique gains high acceptance among clothing industry.

2.2.2 Principle/Method

For the bean dyeing technique, hundreds of individual yarns are wounded parallel to each other around a perforated core beam with flanges on each end (Fig. 2.2). The beam is then loaded into a cylindrical dye vessel that is sealed, so dye liquor can be pumped through the perforations in the beam and then through the yarn. After dyeing, the yarn is washed, extracted, dried, and added to other beams for slashing and weaving.

2.2.3 The advantages and limitations

Bean dyeing has several advantages. Firstly, it can eliminate the crease of fabric. As the fabric is put under controlled tension and wound onto a perforated beam. This can prevent crease in certain level and ensure total control of dimensions of the roll of fabric.

Secondly, the fabric is not able to have any movement in the process of dyeing which means the dyeing method do not apply any mechanical action towards the yarn. As shown in the figure 2.2, there is no movement of the yarn as the hydrostatic pressure of the pump forces the dye liquor through the fabric roll.

Moreover, the machine allows adjustment in water level according to fabric volume. This can give an even and superior dyeing quality. The machine also has an optimized circulation system along with high performance pumps.

However, the yarns need to re-beam after dyeing for weaving because the beaming method is not designed for weaving. More effort and time are needed for weaving process.

2.3 Foam dyeing technology

2.3.1 The background of foam dyeing technology

Foam dyeing technology is one of the surface dyeing technologies for textile. Foam dyeing can develop a novel surface dyeing to cotton fabrics to achieve wash-out effect after garment washing. Although foam dyeing actually gives poor penetration to fiber, it is exactly the wash-out effect which we are expecting. The volume of the dye-liquor is increased by transforming it into foam by injecting air and intense agitation. The increased volume allows the liquor to spread on the fabric evenly even with a small amount of dye liquor

Furthermore, all chemicals used for the traditional treatment of textiles, such as sizing, dyeing and finishing, can be added with foam applying to textiles. Moreover, foam can be applied on products like durables- softening agents, press resins, soil-release products, stiffening agents, flames-retardants, bonding agents and so on. Fabric with different properties such as woven, knitted, lightweight and bulk can be applied on this technology. Even, yarns can be also applied in this method. Therefore, foam dyeing is energy and water saving technology which should be encouraged in industry for protecting the environment.

2.3.2 The history of foam technology development

The development of foam technology started for 1907 by Schmid. He used soap lather to improve batch process for weighting silk and degumming. Fatber and Carroll introduced a foam batch process on textiles materials in mid 1930. Thirty years later, a foam assisted engraved roller printing process was used with different dye classes. This technology could provide the high yields and great economies. It is a specially designed foam applicator that could prevent unstable in the foam density during the printing process. In 1972, a low-liquor-ratio dyeing process, that solvent was emulsified in water, was developed. This process was further improved in 1974, by replacing the water-solvent emulsion with an air-water mixture in a process, which was called the Sancowad batch-dyeing process that used condensation foam. The main advantages of this method were water and energy savings. The technology was highly improved in the early 1980s which have large number of machine manufacturer developed their own foam textile machine for different uses.

2.3.3 Principle/Method

Production of foam must contain water, anionic surfactant and non-ionic block polymer based on ethylene oxide and propylene oxide units. The surfactant is the main foaming agent and also serves as the foam regulator and stabilizer. When they are under a suitable moisture and temperature, the non-ionic block polymer can be able to collapse the foam. It acts as a foam regulator in the steamer.

There are verity of equipment for continuous foam formation such as impellers, special pumps and mixers. Air is dispersed in the liquid with foaming agents so they can disperse by themselves in the aqueous phase. Foaming agents can effectively change the surface tension and elasticity of the bubble wall. The bubble wall should not collapse easily so it has to maintain at certain level of elasticity. Other than mechanical way, foam can be produced by injection of air under pressure

2.3.4 The advantages and limitations

Foam technology is an environmental technology as it saves lots of energy for dyeing or finishing process.

The water consumption is much lower by this method because the generation of foam required less water. Compared with conventional method, it can reduce water consumption for about 30-90%.

Other than water saving, energy from drying and steaming can be saved as well. As the water level of foam technology is lower, less energy are required to dry fabric. It can increase the drying time by 40% and lower the temperature by 38^{o}C. For steaming energy, it can be saved by 50%.

The application of foam technology is flexible as there is no need to purchase extra machine. Foam technology can use with conventional padder. There is no special requirement of the dying chemicals. On the other hand, the chemicals are more fully utilized under this technology.

However, there are several limitations on foam technology.

Pre-treatment of fabric is required for foam dyeing in order to maintain an even wet pick-up ratio of the fabrics. The absorption of chemicals may be inadequate under low pick-up ratio. Some of the chemicals such as softeners, brightening agents and sulphate ions can make unstable foam which may affect the evenness of dyeing result.

Moreover, it is difficult to control levelness and shade for foam technology. It is especially difficult to produce deep shades as there is a restriction on dyestuff solubility and fabric wettability.

There is a problem of maintaining the uniformity of air and liquor in the foam system. It is hard to control the balance between the quantity of foam production and its consumption by the fabric, which may affect the moisture content of the fabric.

2.4 Dyeing process with reactive dye

2.4.1 Introduction

Reactive dyes first produced in 1956 by commercial and were invented in 1954 by Rattee & Stepheness at the imperial chemical Industry. Reactive dye is commonly used in the dyeing of cotton fabric as it is low in price, full shade, easy for application and excellent in fastness.

Reactive dyes belong to categories of cationic dyes. They are used for dyeing polyamide, cellulose as well as protein fibers. Reactive group forms covalent bond with fibre polymer and becomes an integral part of fiber during dyeing. Moreover, reactive dyes can be produced in powder, liquid and even print paste form. It also requires less time and lower temperature in application. These make reactive dyes easy in application. Other than this, reactive dyes have many good properties: They are soluble in water, good in light, washing and perspiration fastness.

2.4.2 Dyeing Principle of Reactive Dye

Reactive dyes consist of a chromophore attached to a reactive group through a –NH- group. It has a relatively small molecular structure and always contains solubilising sulfonic acid groups. Typical chromophores are monazo, anthraquinone, phthalocyanine, triphenodioxazine and formazan. The general structure of reactive dyes is D-B-G-X. Fig. 2-1 is an example of reactive dyes' chemical structure

This type of dyes includes a reactive group which will react with the hydroxyl group in cellulose and form a covalent bond. During the reaction of the dye with cellulose, a certain amount of the dye reacts with water. This removes some reactive groups from the dye and forms hydrolyzed dye. The above reactions occurred under the alkaline condition like soda ash or caustic soda

2.4.3 Dyeing process for cotton fabrics

Among different types of dyes, reactive dye is one of the best dyes to apply on cotton fabrics. This is because the dyeing process of reactive dyes is simple. Also, it has many choices of colours as well as its good colour resilience

Basically, dyeing process for cotton with exhaust dyeing system can be divided into two types: method of salt addition step by step and method of Salt-at-Start. The first method is suitable for all dyeing colours and machine in which dyeing solution does not have circulation such as Winch machine. The second method is more compatibly applied for dyeing colour from medium to depth colour and for machine with dyeing solution circulation. Examples are padding machine, jet dyeing machine and jet flow machine.

After dyeing process, we need to wash out the unwanted dyes on the fabric surfaces. There are three steps in total for washing process. They are hot rinsing, soaping and another hot rinsing.

The first hot rinsing before soaping process is to eliminate or drop concentration of salt and alkali as many as possible. Then, it can avoid the precipitation of reactive dyes and wrinkling lines at fabrics from the degradation of dyeing temperature solution. The second step, soaping, is to eliminate the hydrolyzed dye. It can also increase the power of reactive dye diffusion to exit from surface of fibre. The last step is hot rinsing again. This is to prevent reactive dye pickings from returning to fabric surface, especially back staining.

The last process is fixing. It is suggested to use fixing agent for medium colour and deep colour to strengthen strong tying dye on the fiber and fabric. Fixing agent can enlarge reactive dye molecule in the fiber to lower their migrating property

2.4.4 Factors Affecting Dyeing Reactive Dye

There are some factors influencing the dyeing, exhaustion and fixation of reactive dye.

1. The pH of the dye bath

The pH does not have significant effect on the exhaustion of dye into fabric, but it is very important for fixation. Normally, the optimum pH value of dye is 10.8 to 11.0. If the pH value is high than 11, it will reduce the reaction rate and the efficiency of fixation, and at the same time increase dye hydrolysis. If the pH value is too low, it will have the incomplete fixation. To attain the required dyeing pH, different kinds of alkalis are used, such as sodium silicate, soda ash, caustic soda and their combination

2. The temperature of dyeing

Temperature affects the rate of physical and chemical processes in dyeing. The affinity of the dye for the fiber decreases with temperature and, together the rate of hydrolysis of the dye increases with temperature so the high temperature does not favour the fixation of colour yield. However, increasing temperature increased the diffusion rate of the dye in the fiber so better dye penetration, better levelling and easier shading can be achieved. If the temperature is lower than 20 ^{o}C, the rate of fixation will be very low. As a result, maximum fixation is at the optimum temperature and changing in temperatures affects the dyeing quality

3. The time of dyeing

Generally, increasing time can increase the final exhaustion and levelness. The reactivity of dye and depth of shade decide the time of dyeing. Longer time can obtain deeper shades.

4. The liquor ratio

Decreasing liquor ratio can increase the exhaustion and colour strength, so increase in the liquor ratio lowers the final exhaustion. But, the rate of fixation of most of the dyes is not significantly influenced

5. Effect of Dye Concentration

Increasing dye concentration reduces the final exhaustion so the rate of exhaustion tends to be slow at high dye concentration. However, the fixation rate of the dyes is not significantly affected (Ip, A.W.M., Barford, J.P. & McKay, G., 2009).

6. The concentration of electrolyte

The addition of electrolytes tends to promote the final exhaustion, the rate of exhaustion and dye aggregation, and at the same time decreases the diffusion rate. When salt concentration reaches a critical concentration, the effect will stop. If salt is excessive, there will be “salt-out” of the dye. Using salts has no effects for fixation of dye to fabrics.

7. Surfactants and other auxiliaries

Cellulosic fibres with the aid of suitable surfactants can enhance the dye uptake. For instance, cationic surfactants can change negatively charged fiber to positive charge in order to exhaust dyes. Anionic surfactants can also obtain a high dye uptake. Yet, non-ionic surfactants may decrease the dye exhaustion and colour yield, and cause a change in the shade .

2.5 Molecular sieve structure

2.5.1 Introduction of Molecular Sieve

Molecular sieve is a material with tiny holes of precise and uniform size. It is crystalline metal aluminosilicates having a three dimensional interconnecting network of silica and alumina tetrahedra. Molecular sieve can be made of clays, aluminosilicate minerals, microporous charcoals active carbons, porous glasses, zeolites, or synthetic compounds. The holes of molecular sieve only allow small molecules to pass through and at the same time block large molecules from getting in

Molecular sieve can be classified by its pore size by the unit of Angstroms (A), such as 3A, 4A and 8A. Different size of pore can absorb water and exclude different materials that have larger molecular size such as aromatics and carbon dioxides. In manufacturing level, the size of pore can be controlled in order to block the selective molecules. Therefore, the uses of molecular sieve are wide such as desiccants, silica gels and activated charcoal

2.5.2 Properties and use of molecular sieve

Molecular sieve can absorb gases and liquids. For small molecules, they can pass through the pores and being absorbed while for larger molecules, they cannot pass through it and being blocked form the surface. It has similar function of filter but it operates on a molecular level and traps the absorbed substance.

As water molecules are small enough to pass through the pores, it will be forces into the pores which act as a trap for the penetrating water molecules. Molecular sieve can absorb water up to 22% of its own weight. It can hold moisture well even in the temperature up to 230^{o}C. Molecular sieve can ring the relative humidity in the air as low as 10% RH with its high affinity for moisture.

Another property of molecular sieve is modifiable size of pores. Molecular sieve is a man-made chemical, different materials used in the production can have different size of pore for the tracking and blocking selective molecules.

Due to these properties, it has different use according to the size of molecular sieve. 3A molecular sieves have pores size of 3A. It is used to dry dehydration solvents for electron microscopy. 5A molecular sieves have larger pores than 3A; they are use in desiccation and purification of air, dehydration and desulphurization of petroleum gas and natural gas. Generally speaking, the larger the size of pores is, the more water can be absorbed.

2.5.3 Limitation of molecular sieve

The cost of molecular sieve is slightly higher in cost per unit as it is a mad-made material rather than naturally occurred. Therefore, use of molecular is not widely spread in different industries. Also, Food and Drug Administration (FDA) has not yet approved for the direct contact with consumable items. Use with pharmaceuticals is forbidden in United States. Industries are suggested to have independent testing to meet all government requirements before use. However, they are not willing to fund the expensive testing for approval. This largely limited the usage of molecular sieve.

Although molecular sieve has not approved for safety direct contact, we can use other contactable materials such as resins and softener to construct similar structure as molecular sieve in the use of garment materials. If we can control the size of pores to block specific dye molecules, we can produce wash out effect on garments.

2.6 Resin properties

2.6.1 Background of Resin: DMDHEU, Knittex® CHN

Resin in the most specific use of term is a hydrocarbon secretion of many plants. It can be a natural or synthetic compound that begins in a highly viscous state and hardens with treatment. Resin is classified into a number of different categories depending on its exact chemical composition and possible uses. It is valued for its chemical properties and associated uses, such as the production of varnished, adhesives and even food glazing agents. In garment technology, resins are widely used in garment finishing, such as crease resistant finishing, easy-care and durable press finishing. In this project, two different resins will be tested to construct molecular sieve structure on the cotton surface. They are Dimethylol Dihydroxyethylene Urea (DMDHEU) and Melamine- formaldehyde resin (TMM). Both of them are belonging to cross-link type resin. This type of resin chemically reacts with fibers and cross-links the fiber molecules.

<u>Dimethylol Dihydroxyethylene Urea (DMDHEU)</u>

DMDHEU is mainly used in crease resistant finishing in cotton. The reason of cellulosic fabrics creasing primarily due to breakage of interchenic hydrogen bonds throughout mechanical deformation and an associated bad crease recovery ability, particularly under wet conditions while the creases are ‘‘locked-in’’ during the new hydrogen bonds forming in the dried fabric.

There are three main features for DMDHEU. First, it has low to very low reactivity when ether modified. It has exceptionally good durability and laundering. It is little chlorine retention. It has acceptable level to very low level of formaldehyde release. It is possible to post curing in treatment. It has acceptable laundering durability and hydrolysis resistance (Marsh, J. T., 1966).

<u>Melamine- formaldehyde resin (TMM)</u>

Melamine-formaldehyde resin is a hard and thermosetting plastic material made from melamine and formaldehyde by polymerization. It was initially discovered by William F. Melamine-formaldehyde resins are very resistant to both heat and chemical staining than urea-formaldehyde systems. In the cross-linked form, it provides a useful thermoset plastic. This resin is transparent and colourless which is different from phenol-formaldehyde systems. Melamine-formaldehyde resin has high laundry durability which is suitable to apply on textile. Also, it has synergistic effect with phosphorus flame retardants.

Melamine- formaldehyde resin is not only used in textiles finishes, but also surface coatings and moulding materials. Knittex® CHN which is used in this project is one of the Melamine- formaldehyde resin trade marked by Huntsman Limited. It is a cellulose cross-linking resin for crease resistant finishing.

2.6.2 Structure of Resin

2.6.3 Principle/Method

The main principle of resin is cross-linking. With the presence of heat and catalysts, such as magnesium chloride ($MgCl_2$) or zinc chloride ($ZnCl_2$), these N-methylol compounds react readily with the hydroxyl group of adjacent cellulose chains, forming the desired cross-links. However, heat and acid used to cause the cross-linking reaction which will cause weakening of the fabric and shortened wear life.

Cellulosic fiber such as cotton generally has problem of creasing. This is because cellulosic fiber is configured by amorphous and crystalline region. Also, there are intermediate region exits. Cellulosic chains aligned parallel and closely in crystalline region. This does not allow chains to move and access while cellulosic chains in amorphous and intermediate regions are randomly aligned by hydrogen bonds temporarily and weakly in which are prone to distortion force.

Creases or wrinkles formed are caused by bending fabrics. The force breaks the hydrogen bods between molecular chains in the amorphous region of the fiber. Then, chains will slip pass each other forming creases.

Resin reacts with cellulosic molecules to crosslink with each other strongly. The reformed bonds can prevent chains from going back to their original positions when applying force, water or removing disturbances. OH group of cellulose molecules cross-linked with each other with the removal of water molecule under resin application (Fig. 2.3).

2.6.4 Side effect of resin

For DMDHEU resin, the reaction of DMDHEU must be motivated by catalysts such as magnesium chloride. However, these chemicals will result in degradation of cellulose, and reduce the tensile and tearing strength of cotton fabric. When adding catalyst, different concentration, temperature and time will cause different magnitude of fabric strength loss. Moreover, the reaction process of DMDHEU causes cross-linking, it will make molecules link tightly together so that it will also affect the tensile strength in some degree.

Alkali treatment can remove DMDHEU from a finished fabric. When putting a DMDHEU finishing fabric in alkali treatment, hydrolysis will remove the cross-links. Then, fabric strength can be recovered. However, the degradation of cellulose is not reversible upon hydrolysis of cross-links (Harifi, T. & Montazer, M., 2012).

For Knittex® CHN, the side effect are yellowing made by chlorine bleaches, stiff fabric hand and especially happened in tri-products. Most important, this resin has high formaldehyde release which may cause health problems

2.7 Softener properties

2.7.1 Background of Softener

Softener is the most commonly used chemicals in the garment finishing. It is also called fabric conditioner in home furnishing. It is the most essential textile chemical for after treatment because it provides a high quality image for a garment. Softener can provide an agreeable, soft hand, smoothness, more flexibility and even better drape and pliability.

In the process of preparation and production, textiles become embrittled because of the removal of natural oils and waxes. Softener can solve this deficiency and even provide better hand feel than original. Other than soft hand, softener can provide sense of additional fullness, antistatic properties and better sewability.

2.7.2 Structure of Softener

For the most part softeners comprise molecules together with a hydrophobic and a hydrophilic part. As a result, they are being found intensely at the surface of fibers which is also called surfactants. It is a kind of surface active agents. Generally, softeners have low water solubility hence; softening products are usually sold in the form of oil mixing into water in emulsions containing 20–30 % solids. The molecule of softener usually have a long alkyl group, sometimes branched, of more than 16 and up to 22 carbon atoms, but most have 18 corresponding to the stearyl residue. Other than this molecular structure, softener has particular categories of silicones, paraffin and polyethylene. About one-third of the softeners used in the textiles industry are silicone based (Hussain, T., Ali, S. & Qaiser, F., 2010).

2.7.3 Principle/Method

Softeners normally work on the surface of the fibers. Small softener molecules enter the fibre and supply an internal plasticisation of the fibre forming polymer by reducing of the glass transition temperature Tg. The physical arrangement for the standard softener molecules on the fibre surface is essential. It depends on the ionic nature of the softener molecule and the relative hydrophobicity of the fibre surface

Cationic softeners orient themselves with their positively charged ends toward the partially negatively charged fibre (zeta potential), creating a new surface of hydrophobic carbon chains that provide the characteristic excellent softening and lubricating properties seen with cationic softeners.

Anionic softeners, on the other hand, orient themselves with their negatively charged ends repelled away from the negatively charged fibre surface. This leads to higher hydrophilicity, but less softening than with cationic

For non-ionic softener based on paraffin and polyethylene, the orientation depends on the nature of the fibre surface. The hydrophilic portion of the softener is being attracted to hydrophilic surfaces while the hydrophilic portion of softener is being attracted to hydrophobic surfaces. They show high lubricity (reduced surface friction)

2.7.4 Side effect of softener

The common disadvantage of chemical softener is reduction in crock fastness, yellowing of white fabrics, and change in hue dyed goods and fabric. Softener attracts soil more easily. It may cause yellowing when disclose to high temperature and may negatively affect the light fastness of reactive dyes and direct dyes.

Softeners also bring environmental concern. Most of the softener use petroleum-based chemicals which are a non-renewable resource and are not easily bio-degradable. Also, softeners contain chemicals that are impregnated on fabric and are released over time. These chemicals may come in direct contact with the skin.

Human may absorb or inhale it. Some of the softener ingredients will release formaldehyde. This has risk of having cancer under laboratory tests.

2.8 Pad-dry-cure method

2.8.1 Background

Pad-dry-cure procedure is the most commonly used method for finishing, especially easy-care and durable press finishing. a number of the dyes can be dissolving in the water can be used in this method for dyeing process as well. During the process, we can add catalyst, softener, reactant and other component directly into the bath and pad on a dried fabric. Cross-linking reaction will occur at the stage of curing. If the finish is cured directly after drying, at the same time the fabric is still in an open width configuration, the finish is classified to as a 'pre-cure' finish; the finish is cured before garment manufacture.

2.8.2 Structure

In the manufacturing level, pad-dry-cure process is done in a continuous process which is shown in fig. 2.4. In the lab, it may be done with separate machine. However, the steps are the same. First, a piece of dried and clean fabric is rolled into a bath containing the chemical solution for finishing. Fabrics absorb certain amount of solution, pass through a pair of roller to squeeze out extra solution and make the fabric absorption evenly. The roller can give specific tension to the fabric in order to control the pick-up ratio. Then, fabric will be dried in an oven that has lower temperature. In this oven, they aim at remove the liquid on the fabric so the temperature must be under 100^{o}C. After few minutes, fabric will be dried and go to the curing oven. This oven will set a higher temperature for cross-link process. It is normally higher than 100 ^{o}C, depending on the types of chemical. Finally, fabric will be taken to wash and remove the chemical particles on the surface.

2.8.3 Factors affecting the quality

There are several factors affecting the quality of finishing. They are temperature used in drying and curing process, wetting ability of the fabric and the tension used in the padding process.

Temperature used in the drying process should be under the Tg of the chemical solution. Otherwise, cross-linking process will be done in advance of this process under wetting condition. This may make the reaction not even. Too high temperature may also affect the structure of the fiber, especially cotton fiber, as it cannot withstand high temperature. The temperature of curing process should be higher than Tg of the chemical solution so that it can motivate the cross-linking of the chemicals. However, too high may destroy the molecular structure of the chemicals and fiber which will affect the handle of the fabric.

Wetting ability directly affects the amount of chemical absorbed. If fabrics do not wash before the process, oil or waxes may affect the absorption of solution and hence the concentration of solution pick up. Therefore, most of the solution will add certain amount of wetting agent to help the absorption. In the manufacturing process, the time of fabric dipping in the bath is fixed. They have no choice to re-dip solution. Therefore, controlling the fabric absorption is important.

The tension used in the padding process is to control the pick-up ratio of the solution to fabric. We can set different pick-up ratio by putting different tension on the pad roller. The tension should be even in the whole process. However, knitted fabrics are stretchable in nature, and this makes result uneven in under tension. Knitted fabric may also be distorted during the process of rolling. Therefore, pad-dry-cure method is not advised to knitted fabric.

3.1 Preparation on cotton fabric

One hundred per cent weaving cotton fabric, which is bleached, desized and manufactured by Tsang Kee Fabric Ltd., was prepared for the laboratory testing.

80 pieces of cotton in size of 20cm X 20 cm were prepared for finishing and dyeing. Two different colours of blue and yellow were dyed under three different chemicals. For each chemical and colour, 10 specimens were dyed and treated and 10 specimens without any treatment were needed for control.

3.2 Finishing procedures

3.2.1 Introduction

Three kinds of solution including DMDHEU resin, Knittex®CHN and softener were prepared separately. These three chemicals aim at constructing a surface coating on the cotton yarn in order to block reactive dyes pass through the inner of the yarn. Pad-dry cure method was used for finishing treatment. This is the fastest and most convenient method for garment finishing. Also, this method is suitable for these three kinds of chemicals. Magnesium chloride is the catalyst for DMDHEU resin and Knittex resin. It is an acid catalyst for the reaction of resin. For the consistent of the finishing, temperature and time of drying and curing should keep constant for the three chemicals. For each chemical, 20 pieces of specimen were treated for next procedure which is reactive dyeing.

3.2.2 Apparatus/chemicals

- Horizontal Padding Machine

- Drying and curing machine (Mathis Lab Dryer)
- Hydro-extractor

3.2.3 Experiment procedures

Recipe of three kinds of finishing:

Solutions of three finishing were mixed according to the above recipe. There are 10 pieces of specimen for each finishing, 1L of solution were mixed. After the preparation of solution, pull some solution between two rollers and let the rollers rotate in order to wash the rollers. Open the rollers by pushing the hand rail to release the washed solution. Close the rollers again and pull some solution between them. Put the fabric between rollers. Specimen absorbed solution in between the rollers and padded out excessive solution. Specimens were padded at pick-up ratio of 80%. Then take out the specimens and take it to dry and cure into curing machine. The treatment was followed the below treatment condition.

After drying and curing, the finishing process was completed. Repeat the above process for Knittex resin and softener. The treatment condition for the other finishing is same.

3.3 Dyeing Procedures

3.3.1 Introduction

Reactive dye was selected for the dyeing test. Two different colours were chosen for data analysis. They are light colour: yellow (Yellow S-3R) and dark colour: blue (Ocean S-R). Both of the reactive dyes were manufactured by Huntsman. The dyeing method of reactive was same as finishing which was pad-dry-cure method because it is a fastest method compared with dye bath method. For each colour, 10 pieces of specimen were dyed for each kind of chemical. There was a control sample dyed without any treatment. Thirty-one pieces of specimen for each colour were prepared for testing procedure in this step.

3.3.2 Apparatus/chemicals

- Horizontal Padding Machine
- Drying and curing machine (Mathis Lab Dryer)
- Hydro-extractor

3.3.3 Experiment procedures

Recipe of reactive dyeing (Same for both colours):

Prepare the dye solution of blue colour and yellow colour according to the above recipe. 3L of solution was prepared for each colour and each kind of finishing specimen used 1L of solution. Firstly, wash the roller same as mentioned above.

Pad specimen with the similar method mentioned above but the solution changed to dyeing solution. Put the specimen to drying and curing machine. Treat in the condition according to below table (A.K. Roy Choudhury, 2006).

For each colour, one more specimen was dyed without any finish treatment for the purpose of control. After drying, all specimens washed in the tape water to wash out extra dyes on the surface. Dry the specimen in drying machine and dry under room temperature.

3.4 Fastness Testing (Colourfastness to laundering: Accelerated)

3.4.1 Introduction

Colour fastness of washing is important for this project. It is because denim was expected to have certain level of washing out effect during home laundry. Therefore, customers are able to tolerant higher level of colour loss and staining for denim products. Colour fastness of washing was tested according to the standard of AATCC Test method 61 Test No. 1A from 2011.The test was demonstrating the condition of “five hand”, home or commercial washing with detergent WOB and abrasion action from stainless steel balls. Test No. 1A is to evaluating the colour fastness of textiles that are accepted to withstand repeated hand laundering at low temperature. Specimens subjected to this test should show five typical careful hand launderings at a temperature of 40+/-3^{o}C.

3.4.2 Apparatus

- Atlas launder-ometer

- 75mm X125mm level lock stainless steel canisters
- Stainless steel balls (6mm in diameter)
- Grey scale for assessing staining

3.4.3 Sample preparation

Samples with size of 10cm X5cm were sewn with a multi-fibres test fabric face to face along the four edges. This can ensure the contact and abrasion between samples and multi-fiber test sample.

3.4.4 Experiment procedures

Each sewn sample was put into separate stainless steel canister. Add appropriate amount of water, detergent and stainless steel balls into the canister according to the following table. The detergent used was ECE Detergent (B) FBA-free. Then, lock the canister to ensure no liquid come out during the whole process of washing. Put all canisters into Atlas launder-ometer for washing and set temperature in 40 oC for 45 min.

After washing, raise the sample under tape water and dry the multi-fibers and samples. The final step is assessment of the multi-fiber. Observe the staining on multi-fiber in 45^{o} under D65 light which is day light with AATCC Grey Scale for colour change. The grey scale consists of 9 pair of standard grey chips. Each pair represent a different colour contrasts in shade and strength. Rate the staining level according to the corresponding numerical fastness rating. Grade 5 means negligible or no colour transfer. Grade 4.5 means colour transferred equivalent to scale 4-5 on the Grey Scale for Staining. It is to find out the matching staining on the corresponding scales.

3.5 Fastness Testing (Colourfastness to crocking)

3.5.1 Introduction

Colourfastness to crocking is to determine the amount of colour transferred from the surface of sample to other material surface by rubbing. It is also important to denim product because some of the wash-out effects are done by physical abrasion. Same as colourfastness to washing, denim product has larger tolerance on colour staining. The test was based on standard of AATCC Test Method 8 in the year of 2008. Both wet crocking and dry crocking were tested for each colour and chemicals. The results were compared with the control samples.

3.5.2 Apparatus

- AATCC crockmeter (Model: M238AA)
  - 5 cm x 5 cm white cotton test cloth
  - Grey scale for assessing staining

3.5.3 Sample preparation

Two specimens was used, one each for the dry and the wet tests. Cut specimens at least 50 X 130 mm.

3.5.4 Experiment procedures

First, lock the cotton test cloth (either wet of dry) with a ring on the crockmeter. Put the sample on the crockmeter in flat position and cover it with specimen holder to fix the sample. Rotate the arm of crockmeter by 10 times at the rate of one turn per second to slide the covered finger back. Finally, take out the cotton test cloth and assessed with grey scale. For wet crocking, cotton test clothes were wetted with distilled water and squeezed or hydro-extracted to a pick-up level of 100%. The cotton clothes were dried under room temperature before assessment. The assessment method is same as colour fastness to washing mentioned above.

3.6 Colour Strength Test (Kubelka-Munk Theory)

3.6.1 Introduction

The Kubelka–Munk colour model describes the reflectance of coloured sample as a function of absorption spectrum K(λ), a scattering spectrum S(λ) and the reflectance spectrum of the substrate.

The basis of computer colour matching is built upon the theory developed by Kubelka-Munk in 1931. The quantities of radiant energy absorption and scattering can be defined by the coefficients of K and S respectively. The following equation shows the relationship between reflectance value and Kubelka-Munk coefficients at a certain wavelength in its simplified form: $K/S=(1-R)^2 / 2R$ (simplified formula for fully) opaque object where K is the coefficient of absorption; S is the coefficient of scattering; and R is the absolute reflective factor.

The simple Kubelka-Munk relationship applies only to those materials that are fully opaque. The relationship indicates that if the total absorption in the material increased without changing the total scattering, the reflectance will decrease. In contrast, if the total scattering is increased without any change in total absorption, the reflectance will increase shows the relationship between K/S and the reflectance (R).

In addition, the quantity K/S is linearly to the concentration of colorant in substrate medium. If black is added in the colour, it means a higher K will be obtained and the substrate absorbs strongly, lower reflectance and a darker shade will be obtained. If white is added, the scattering is stronger. Then, the reflectance will be increased and a lighter shade will be obtained. Therefore, higher dye uptake of the substrate will have a higher quantity of K/S value.

In other words, K/S value can show the colour strength and dye pick up. Test is conducted to evaluate the colour pick up changes after applying different chemicals.

3.6.2 Apparatus

- Colour-Eye 7000A from Gretag Macbeth

3.6.3 Experiment procedures

3.7 Colour measurement test (CIELAB International Formula of Colour Difference)

3.7.1 Introduction

Colour is difficult to describe objectively as weight or length because it will change under different light source, observer and object reflectance. The CIE (International Commission on Illumination) system is one of the most widely accepted systems by all colour related industries. CIE system can use computer system to describe and measure the colour difference by formulas. It is a fair standard for comparison. For describing a colour, they use three values of X, Y and Z. For measuring colour difference of two colours, they use by the values of ΔL, Δa and Δb. the computer system can also generate vale of Δc, Δh and ΔE by formula. In this project, we need to compare the colour change in dyeing effect before finishing with after finishing.

Colour difference- CIE L*a*b* values

The above figure (Fig.3.4) shows the model of CIELAB system and the meaning of the values is explained below.

ΔL- It is a value that shows the difference in lightness/ darkness between standard and submit. A negative value means a shift to darker (black) while a positive value means a shift to lighter (white)

Δa- It is a value shows the red/ green colour difference. A negative value means more green and positive value means more red.

Δb- It is a value shows the yellow/ blue colour difference. A negative value means more blue and positive value means more yellow.

Δc- it is a value shows chromaticity difference, difference in brightness or dullness. Negative value means less saturated (paler) than the standard while positive value means more saturated (richer/ brighter) than the standard

Δh- It is a value shows difference in hue or shade. It represents the angular difference (in degrees) between the standard & batch

ΔE- It is a value shows the total colour difference. It means the total colour difference between two points (standard colour & batch). The closer the two samples, the closer the colour. The total colour difference, ΔE, cannot tell us the complete information about the nature and magnitude of colour difference. Thus the difference in value of L*, a* and b* should be calculated.

3.7.2 Apparatus

- Colour-Eye 7000A from GretagMacbeth

4.1 Result Evaluation

Since the aim of the research is to develop a surface dyeing technology with desirable wash out effect similar to denim fabric, a lot of results achieved from the three chemical solutions will be discussed in order to determine which chemical is suitable for construct a structure similar to molecular sieve.

4.1.1 Appearance/Quality of sample

Ten pieces of specimen from each type of finished specimen, including DMDHEU, Knittex® CHN and softener, are dyed with reactive dyes with one more for control. The above figures, Fig. 4.1 and 4.2, show the dyeing effect of yellow and blue reactive dyes without and with finishing. All of the colours are dyed evenly but different finishing resulted different shades. The left hand side is the sample for control which is purely dyed with reactive dyes only.

Both yellow and blue samples treated with softener have closest colour shade with control sample. Samples finished with Knittex® CHN have the lightest colour shade when compared with control. They have a dull colour effect. DMDHEU finished samples also have light colour shade when compared with control but they are slightly deeper in shade colour than Knittex® CHN samples. The yellow samples have larger difference in DMDHEU finish with Knittex® CHN.

The colour shade of a fabric highly depends on the wet pick-up ratio. Insufficient pick-up can lead to inadequate, non-uniform and unlevelled absorbency. All samples were dyed in pick-up ratio of 80% which is a high ratio and can give out deep colour. However, the result showed that resins and softener can affect the shade of colour even dyed with same pick-up ratio. Resins of DMDHEU and Knittex® CHN have largest effect on the dyes absorbency.

As both DMDHEU and Knittex® are resins, the treated samples have harder handle compared with controls while softener treated samples have better handles than controls. The crosslinking reaction makes cotton fabric more stiff and hard in handle. Also, the resin on the surface may affect the dyeing quality if resins were unevenly padded. Some area with more resin will have lighter colour. Therefore, to have evenly dyeing result, we should ensure even resin padded on fabric.

For softener, the dyeing qualities of samples are much better than others. As the function of softener is giving smooth handle, its sample has better handle than control. Also, the dyeing quality is as good as control.

4.1.2 Washing colourfastness

Below are results of yellow colour washing colourfastness:

From the above data, we can see that reactive dyes have very excellent fastness to washing especially acetate, nylon, silk, viscose rayon and wool. Reactive dyes of both yellow and blue colour do not have any staining to these materials. As yellow colour is a light colour, the non-staining performance of yellow sample is slightly better that blue colour on average. Reactive dyes were observed to have average grade of 4 in cotton staining.

Specimens treated with DMDHEU, Knittex® CHN and softener did not affect the staining of acetate, nylon, silk, viscose rayon and wool. All of the results stay at grade 5.

For DMDHEU resin, results showed that staining to cotton become less after the finishing. The grade changed from 4 to 4.5 for yellow colour and half of the blue colour specimens had grading of 4.5 as well. It seems that DMDHEU resin has improved the washing colourfastness but that is not the aims of the project. We are expecting colour washing out during laundry just like denim. However, as the shade of the colour is lighter, which means that less reactive dyes are stick and absorb in the fabric. As a result, less staining on other materials is reasonable. That's why light colour clothes have less colour staining in home laundry.

For Knittex® CHN resin, it also showed improve fastness to washing. Both of blue and yellow specimens have average grading of 4.5. The reason may be same as mentioned in DMDHEU resin. As the colour shade of specimen finished with Knittex® CHN is even lighter than DMDHEU resin, it is reasonable to have better result of fastness to washing

For softener, the washing colourfastness is same as control on average, which means the softener, does not have effect to the washing colourfastness.

4.1.3 Crocking colourfastness

Below are results of yellow colour washing colourfastness:

From the above data, we can see that reactive dyes have very excellent fastness to rubbing especially dry rubbing (Grade 5). Wet rubbing is grade 4.5, which is also a very good performance. After applied different finishing, the change of fastness to rubbing performance depended on different chemicals.

For Knittex® CHN resin, the performance of both wet and dry rubbing is same as the control specimens. The wet and dry rubbing fastness of DMDHEU treated sample slightly downgraded by 0.5, compared with control specimens. It shows that

DMDHEU treated sample does not react well with reactive dyes so that the dyes do not stick firmly with DMDHEU.

For softener treatment, it affects wet rubbing result only. The fastness to rubbing changed from grade 4.5 to grade 4 but there are no changes on dry rubbing. This is because softener is easily to wash out by water. Reactive dyes are rubbed out with softener when there is water.

4.1.4 K/S Value

The relationship between colour strength (K/S value) (sum of the K/S value of wavelength from 400 to 700 nm) and the reflectance value can be described as $K/S = (1-R)^2/2R$. Colour strength values (K/S) were calculated according to AATCC Evaluation Procedure 6-2008 Instrumental Colour Measurement.

Below figure 4.5 and figure 4.6 showed the result of yellow colour and blue colour for different finishing respectively.

According to Kubelka-Munk Theory, higher the K/S value, higher the dye uptake and dullness of the fabric will be. For the yellow colour, the wavelength is at about 600nm and we should compare the colour strength on the wavelength in highest K/S value. It is 600nm potted in the figure 4.5. For the blue colour, the wavelength is at about 400nm and we also need to find out the highest K/S value for comparison. It is located at 440nm which is potted at figure 4.6.

From the two figures, it showed that the colour strength decreased when resin finishing applied on the specimen. For yellow colour specimen, K/S value decrease 75% compared with control specimen when treated with DMDHEU. K/S value decrease 92.4% compared with control specimen when treated with Knittex® CHN. Colour strength decrease more when applied on Knittex® CHN. For blue colour specimen, K/S value decrease 91.2% compared with control specimen when treated with DMDHEU. K/S value decrease 98.9% compared with control specimen when treated with Knittex® CHN. Colour strength decrease more when applied on Knittex® CHN for both colours

The result showed that both kind of resin have significant resistant effect to reactive dyes and hence decrease the colour pick up. This makes the specimens paler in colour shade.

However, softener treated specimens do not showed large variation in colour strength. The K/S value curve is almost the same with control. This showed that softener do not have resistant effect on reactive dyes.

4.1.5 Colour measurement

Results of colour difference measured from CIELAB system are showed from the following scatter diagrams. Colour differences are compared with the control specimens.

Delta E value in CIELAB system shows the total colour differences of the compared colour. Higher values mean higher level of difference. From the diagram, we observed that two kinds of resins have effect on colour quality but there is no significant change for softener specimens.

Knittex® CHN resin specimens have the largest overall colour difference with control specimens for both yellow and blues dyes. However, yellow colour specimens treated with Knittex® CHN have larger difference then blue specimens.

Softener specimens stay at acceptable range of colour difference for both yellow and blue colour. The differential level of both colours is also the same. This means that softener treatment does not affect the colour effect and quality for both light and dark colour shades.

DMDHEU resin has middle colour changes among three chemicals, ranged at about 20 to 30. Both of light colour and dark colour has similar level of colour difference. This showed that the DMDHEU resin has a constant effect on the colour difference.

However, delta E value is an index showing the level of colour difference but cannot tell how it changes. CIELAB system has other values tell more about the change of colour, which are delta a and delta b values showed in the following diagrams (Fig. 4.8)

Below are figures showing data of delta a* and delta b*:

By observation in the above diagram, we can find a pattern of colour change affected by the chemicals. For yellow specimens, specimens approaching to greenish blue after treated with Knittex® CHN resin in a larger extend compared with other chemicals. Specimens were approaching to greenish yellow in a smaller extend after treated with DMDHEU resin. Softener can be said as no colour difference as mention above. Therefore, data is located near to 0. For Blue specimens, both of the resin treated specimens were approaching to yellowish green. Knittex® CHN has larger extend of colour difference compared with DMDHEU resin.

Moreover, there is a common feature observed from the two colours. Both DMDHEU resin and Knittex® CHN resin made more colour lose for their original colour. That means for yellow specimens, all resin treated specimens lose more yellow colour and blue specimens lose more blue colours. Other than telling colour content changes, lightness is also an important affect to assess colour changes. Below diagram shows the changes of lightness.

Specimens of softeners do not have large effect in lightness. Specimens from DMDHEU resin of both colours have middle level of lightness changes while Knittex® CHN resin has largest effect on lightness. All of them are positive values and it means that the colour changed to lighter compared with control specimens. This explained why the resin treated samples are paler.

To conclude, there are no significant changes in colour for softener treated specimens but resins have made specimen pale and dull. There is chemical reaction for fabric and resins so resins have affected the colour quality and appearance. More details will be discussed in later parts.

5.1 Conclusions

The above data, it is showed that both of the commercial cross-linking resins (DMDHEU and Knittex® CHN) can construct an outer layer on the yarn surface to block the dye stuff getting in. Both resins can reduce the dye concentration and colour shade in certain level shown on colour strength and colour difference test. The report showed that commercial resins can give similar effect in blocking colour into the core of yarn but there is difference with conventional denim washout effect.

As the cross-linking effect is happened in the same level of cellulose instead of on the outer layer of cellulose, the cross-links effect on the fiber molecules is not dense enough to block all dyes. So, there is little colour getting inside the yarn core. The colour difference measurement test showed that resins have certain effects in affecting the colour dyed on the cotton especially when applying Knittex® CHN. The experiment results revealed that cross-linking concept may be suitable to develop surface dyeing if a stronger and denser bond can be constructed.

Although, cross-links from DMDHEU or Knittex® CHN resin can have colour resistant to reactive dyes, at the same time they damage the structure and property of cotton. Finished specimens of both resins are stiff in handle, dull in colour and have less tensile strength. These are the common side effects of resin application. So, it has to take a balance between the resin concentration and resistant effect. Moreover, the dyeing quality was affected if there was uneven distribution of resin coating.

For softener, there is little effect in dyeing quality and wash out effect. As softener composed of long chain molecules, cross-linking softener molecules are not strong enough to block dye stuff shown in the experiment result, specimens treated with softener before dyeing have not much difference with control in the dyeing quality. Reactive dyes can go into the core of yarn evenly which is same as control. The research results proofed that long chain molecules are not suitable for constructing an outer layer for surface dyeing.

Traditional denim fabric requires certain level of colourfastness in order to have desirable wash-out effect. However, cross-linking resins and softener do not affect the colourfastness property of reactive dyed specimens. On the one hand, this showed the treatment will not bring bad effects to dye quality not on the other hand.

To conclude, the research showed that commercial resin such as DMDHEU and Knittex® CHN have certain level in affecting dye pick up and the colour strength. Yet, the results still have difference with real denim. This told that commercial chemicals do not reach the perfect result. There are still more to do on investigating and testing the perfect chemical solution as well as the construction method on molecular sieve structure and a convenient wash-out method.

5.2 Recommendations for future research

In a highly competitive garment market, garments with low dyeing cost and easy finishing process can fulfil customers and manufacturers' wants. Surface dyeing concept is an environmental friendly and cost saving concept to dyeing industry which is worth for developing. In the research, cross-linking concept to construct coating on the surface of yarn before dyeing is innovative. Although the result is not perfect for all chemicals, the testing report showed that the concept is applicable for development. To improve the effect of cross-linking discovered from the research, recommendation has been made for future research.

1. The conception of coating a surface on the yarn surface before dyeing is feasible in application. Results from the research showed that cross-linked resin can block certain amount of dyes into yarn. Future research, if there is, can work on this concept to develop a suitable coating on the yarn.

2. Choice of material for future research should have reaction to both reactive dyes and cellulose molecules in order to have desirable finishing and dyeing effect. The three chemicals chosen from this research have excellent reaction to cellulose and reactive dye is also suitable for cellulose yarn. It will have good dyeing quality if the middle layer materials react with dyes and cellulose.

3. Other technologies, such as nano-technology are suggested to further strengthen the bond of the coating because the “wall” constructed from cross-linking is not strong enough to block dyes getting inside of the yarn for this research. Future efforts may focus on usage of nano particles as filters or cross-linking agents because their small size may be able to enter in between the polymer chains (Harifi, T. & Montazer, M., 2012).

4. The colour shade of specimen treated with resins is dull. It is recommended that future research can take consideration on the colour shade. Most of the garments prefer a wider range of colour shade and sharper colour effects.

5. Reactive dyes were used in this research. It is recommended that other types of dyes such as direct dyes and vat dyes can be used in the future as these dyes are also commonly used for denim fabrics. Thus, the relationship between the dyes and coating materials can be further understood.

6. Apart from colourfastness test and colour difference measurement, wash-out effect, thickness of coating materials and more range of colours can be tested for further investigation on the dyeing quality and effects. Different pick-up ratio and concentration can be tested for investigating the reaction on dyeing.