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The Role of Binders and Its Chemistry in Textile Pigment Printing

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Abstract

This review paper presents the chemistry of binders and their action in pigment printing of cellulosic textile substrate. Printing of textile materials is probably best described as an industrial art, having a long history and an assured future. Textile printing is the most versatile and important of the methods used for introducing color and design to textile fabrics. In pigment printing, insoluble pigments, which have no affinity for fibers, are fixed on to the fibers with binding agents or binders. In textile printing, dyes or pigment are transferred to textile fabric by printing pastes. Binders are the mechanism used to keep the color on the fabric when using pigments for printing textiles. The choice of binders will always depend upon the final fastness requirements as well as the cost requirements of the process. Almost all the binders used in textile pigment printing are the addition polymerization products. The binder is a film forming substance made up of long chain macromolecules, which when applied to the textile together with the pigment , produce a three dimensionally network. Different binders were also developed for the purpose, resulting finally in the use of water- in-oil, and oil-in-water emulsions. This greatly accelerated the use of pigments in textile printing and then pigments have become major coloring matters used in printings. This paper review gives more emphasis on the need and functions of binder in pigment printing and also the chemistry of binders and its action in fixation of the pigment onto the textile substrate.

Keywords: Binder • Pigment printing • Binder's chemical structure • Role of binders • Fixation

Introduction

Coloration is value-added treatments for most textile materials which includes dyeing and printing processes. Dyeing is a process of applying color to the whole substrate. From the view of coloration, printing is a partial dyeing on fabrics to form an attractive pattern. Coloration could be achieved with either dyes, by dyeing or printing in aqueous solution, or with pigment by using a print paste. Pigment printing is not only the oldest but also the easiest printing method as far as simplicity of application is concerned [1-7]. More than 80% of the printed goods are based on pigment printing due to its obvious advantages, such as versatility; ease of near final print at the printing stage itself, applicable to almost every kind of fiber or mixture, and the ability to avoid any washing processes after fixation [4,7-11].

In pigment printing, insoluble pigments, which have no affinity for the fiber and fixed on to the textile with binding agents in the pattern required. This description is perhaps oversimplified, but it does obviously set pigments apart from dyes that are absorbed into the fiber and fixed there as a result of reactions specific to the dye [12,13]. Printing paste is the main constituent of printing which enables the formation of the predefined patterns.The printing paste for pigment printing generally contains pigments, emulsifiers, binders, softeners, thickeners, antifoaming agents, and crosslinking agents [4]. It is therefore necessary to give individual consideration to each of the printing paste constituents. All the above constituents are not used simultaneously in any pigment printing paste depending on the class of pigment used and style of printing employed, suitable component are sleeted in making in printing paste [13-24].

Binders and fixers play important roles in pigment printing achieving optimum fastness properties. During the earlier stages of the development of binders for use in pigment printing polyvinyl acetate was considered a good binder. However, it was realized that it produced too stiff a handle. On other hand acrylate resins gave soft effects but pigments bound with them were not fast to rubbing [13-15].

Currently, pigment printing is perhaps the most commonly and extensively used technique for printing textiles. However pigment printing has a few problems –relatively high temperature cure, stiff hand and poor crock fastness of printed goods. These disadvantages are related to binder used. Thus, to improve the quality of pigment goods, the overall properties of the binders need to be improved. Methods to lower the curing temperature have received the most attention because the high temperature cure process not only wastes energy but also runs the risk of destroying substrates that can't endure high temperature processes [8].

Most pigment printing binders on the market are macromolecule copolymers that are formed by emulsion polymerization processes from vinyl based monomers [16,17]. They contain hydrophilic sections, which make them dispersible in print paste formulations and side chain functional groups, some of which are capable of forming films by crosslinking reactions [17]. Crosslinking is the "glue" that gives structure to binder films which encapsulate and here the pigments to fabrics. Functional groups which usually do not form crosslinks are methyl, ethyl, and butyl acrylates, acrylonitrile, styrene, and ethyl groups, while the groups that react to form crosslinks are acrylamide, methylolacrylamide, hydroxyl ethyl acrylate, acrylic acid, meth acrylic acid, and fumaric acid [16-19]. Many of these groups are hydrophobic and help prevent swelling of the print paste in water.

The use of chemically modified wheat gluten as a binder in pigment print pastes for textiles was investigated that the performance properties needed in textile pigment printing binders for apparel and interior applications could be attained by economical methods of chemical modification. This study improved solubility in alkaline solutions and technical properties resulting from chemical modification of gluten for paper binders [20]. Wheat gluten is composed of two water insoluble proteins found in wheat flour, glutenin and gliadin. Glutenin molecules have linear configurations and the potential to form disulfide and other crosslinks. Gliadin consists of small globular molecules, is soft and has good adhesive properties [21]. Coffman's, J.R. et al. (1951) determine if modified gluten has potential to be a good binder in textile print pastes. This was accomplished by chemically modifying wheat gluten with methyl acrylate using Coffman's procedure, adding the modified gluten to print paste formulations, applying it to fabrics and evaluating the performance [22].

Wazeer H. S. et al. (2012) reported that the crocking fastness properties

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of pigment printed fabric is less than the crocking fastness of the reactive printed cloth, because of insolubility of pigments. However, the crocking fastness can be improved by selecting the appropriate binder. In this study binder F, binder F.T and binder 77 were used for sample printing with three different viscosities and three shades. The light fastness of the fabric printed with binder F is best than the others and the rubbing fastness of the fabric printed with binder F.T is excellent [13].

Najafi et al. (2009) have investigated that some novel prepared aqueous oligomers (binder)of polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-co-propoxylate having zero volatile organic compounds can be used safely for preparing printing paste for screen printing of all types of textile fabrics using pigment dyes. The highest color strength (K/S) is obtained and the fastness properties range between good and excellent for samples printed using polyurethane acrylate based on glycerol ethoxylate-copropoxylate, this is true irrespective of the type of printed fabric. The lowest K/S is obtained in case of using Ebecryl 2002 as a commercial binder. The binder of PUA based on PEG2000 gives K/S better than the binder of PUA based on PEG1000+2000 for all the types of printed fabrics unless in case of printed wool, the inverse is true. The fastness properties of goods printed with this system were satisfactory and the hand of printed goods was soft [23].

Hamilton and Chiweshe (1998) studied that the rubbing fastness of polyester fabric depends on binder elasticity,adhesion on the textile materials, and uneven dispersing of the pigment in the print paste[14]. Yaman NE. et al. (2012)stated that binder was well dispersed and had the same elasticity; these results indicated that plasma treatment improved the fabrics adhesion to printingpaste and also binder. The rubbing fastness results can be attributed to better binder film strength of plasma treated fabrics than untreated fabrics. After plasma treatment, amount of linkage between binder and fibers and resistance of the chemical bonds increased because of increasing polar groups [24,25].

Jiang, Hu et al. (2013) investigated thatvinyl silicone oil (VSO) modified polyacrylate latex is synthesized by emulsion polymerization as a binder for pigment printing.Good rubbing fast nesses and soft handle of the prints are acquired by using the VSO modified polyacrylate core-shell latex particles as binders. Comparison with a certain commercial binder suggests that the VSO modified acrylate copolymer's core-shell latex has a charming expectation of industrial application [25].

Lamminmaki, Kettle et al. (2010) investigated that the inkjet ink penetration speed depends on the used binder type in the coating layer and the level of external pressure, if applied. The polyvinyl alcohol binder can allow diffusion of the inkjet liquid phase, and swells under the influence of the ink. This acts to close the Nano-size pores and therefore slows down the ink penetration speed in the coating structure. Moreover, polyvinyl alcohol dissolves and this may have an effect on the ink properties and binder transport during the penetration process [26].

Different binders were also developed for the purpose, resulting finally in the use of water- in-oil, and oil-in-water emulsions. This greatly accelerated the use of pigments in textile printing and then pigments have become major coloring matters used in printings.For example, the shades produced should exhibits good fastness to light, crocking, washing, gas fading chlorine, Alkalis, perspiration and solvents [7,8,13,14].

In fixation of pigment to textiles by using binders; UV, as well as radiation curing technologies are used in the textile industry, because of low energy consumption, short start-up period, fast and reliable curing, low environmental pollution, curing at room temperature, space saving ,etc [27].

Functions and types of binders in pigment printing

Binders are typically added to printing paste in order to:

- Coat the pigment and allow printing of very fine dispersions,
- Protect the pigment from mechanical abrasions,
- Fix the pigment to the fibers and
- Give the paste good drying properties.

In general binders for textile printing are classified into two as reactive and non-reactive. Non-reactive binders do not contain reactive groups. Due to the absence of reactive groups they do not self - crosslink during fixation or curing. Thus addition of fixing agent is required to form a stable binder film on substrates.Reactive binders contain reactive groups usually from copolymerization with monomers such as N-methyl acrylamide or similar compounds. These binders are able for self-crosslinking and form stable film during fixation [28].

Essential qualities of binders

Binder used in pigment printing must have certain qualities. Binder should not get coagulated due to shear forces operating during printing. If coagulation takes place clogging of the screen and blocking of the engravings of the printing rollers take place during the actual printing. The binder film must be clear, of even thickness, smooth, and neither too hard not soft. It should be elastic in nature, should have good adhesion to the substrate without being tacky. It should have good resistance to chemical and mechanical stresses and should be readily removable from the engravings of the printing rollers, screens, back grays and blankets. Among these properties, one can be improved at the cost of others [14,23].

Good binders must be colorless, odorless compounds that are easily and smoothly dispersed in print pastes without adversely affecting the viscosity and are easily removed from printing equipment, such as screens and rollers. Binders should form flexible films that encapsulate pigment particles and adhere to fabrics without swelling during laundering and dry cleaning [29,30].

Textile binders are necessary to form a matrix to entrap the pigment particle and must be stable to outside forces that would tend to dislodge the pigment from the textile substrate, such as washing or rubbing. A binder must lend itself to application and have other characteristics to enhance the coloring effect of the pigment. Since pigment coloration is an additive effect to the substrate, the components of this addition will tend to change the feel of the substrate or fabric.

Binder traits:

- Inexpensive
- Provide good color yield
- Non toxic
- Soft
- Wash fast
- Provide good crock fastness
- Easily polymerized
- No stain and build up on equipment
- Non-yellowing
- Not affect light fastness
- Be stable in application

Binder chemistry in pigment printing

The binder used in the pigment printing process is usually based on styrene-butadiene, styrene acrylate or vinyl acetate-acrylate co-polymer [11,16]. In the printing process, three dimension binder films have occurred in hot air ambient due to pH changing. Kind and amount of the chemical polar groups of fabrics influence fixation conditions and adhesion strength of the binder-to-fiber bond [31].

Binders are the mechanism used to keep the color on the fabric when using pigments for printing textiles. The choice of binders will always depend upon the final fastness requirements as well as the cost requirements of the process. Choosing a binder forpigment coloration is a complex but critical step in developing a recipe which will meet very specific requirements. The place to start to determine which final fabric properties are important as various end userapplications may require a different polymer to achieve the desired results [18,19,29,32]. Almost all the binders used in textile pigment printing are the addition polymerization products. They are actually polymer type; the structure may be represented as Figure 1 [29,32,33].

Waris Iqbal et al. (2009) has studied that the binder film in pigment print is a three-dimensional structure, the third dimension is rather less important than the other two. The binder is a film-forming sub-stance made up of long chain macromolecules, which when applied to the textile together with the pigment, produces a three-dimensionally network. The links are formed during some suitable fixing process, which usually consists of dry heat and change in pH value, bringing about either self-cross linking or reaction with other suit-able crosslinking agents [11,29,30,32]. The cross-linking reaction must produce covalent bonds, which are insensitive to hydrolyzing agents (washing liquor, perspiration, industrial atmosphere). The reaction should be activated in dry hot air by curing process [34]. While the prints are being dried, a film is formed from the dispersed binder. Its formation takes place in two stages: flocculation (or coagulation) and coalescence. During the first stage of film formation, water and surfactants are removed from the binder by absorption and evaporation. The dispersed solids coagulate to form a gel-like layer of very tightly packed 'balls', which have only poor solidity and adhesive properties. During the second phase, the gel particles flow together to form a continuous film [16].

The reaction between the binders and the cellulosic substrate may be represented as follows in equation (1):

Binder-CH-OR + HO-Cellulose ⇆ Binder-CH-O-Cellulose + ROH

Where R is CH_3or H.

Cross linking increases the crocking, washing and dry cleaning fastness properties, but detrimentally affects the handle of the fabric. When the binder molecule have no self-crosslinking groups, an additional cross linking agent such as urea formaldehyde or melamine formaldehyde condensate, methylated urethane compounds etc, having at least two reactive groups per molecule are added in the binder system [16,35].

Wazeer H. S. et al. (2014) studied that the reaction between the binder and the fiber catalyzed under acidic conditions & that it is reversible reaction. Since methanol or water is a product of the forward reaction, leading to the fixation of the binder onto the fiber, this reaction is favored by the removal of methanol or water. Curing with fresh air at high temperature effectively removes this product and ensures fiber - binder bond formation. Acrylate copolymers have high binding power and are marked by ease of manipulation and are used in almost all pigment printing operations [13,24].

Binders are high molecular weight film forming agents produced by the polymerization of simple intermediates initially present in the paste in a homogeneous, dissolved or dispersed state [24,35]. After evaporation of the solvent or other liquid vehicle, heating produces a thin coherent coating or film. The film, several microns in thickness encloses the pigment particles and adheres to the fiber. The rubbing, washing and dry cleaning fastness of a pigment print are, the incorporation of reactive groups in the macromolecule enables linking to occur within the binder after film formation by a simple heat treatment thereby improving its resistance to chemical and physical agencies. The important monomers used in modem binders are:(1) Derivatives of acrylic acid, especially its esters (2) Butadiene and(3) Vinyl acetate [13,24,29,35].

Different binder systems and their chemistry

Acrylic Binders

The binders have been used in the earlier in pigment printing are not self-cross-linking and the fixation or curing is done in the presence of cross-linkers. These agents facilitate the cross-linking reaction to occur at the curing temperature of 150^{0}C [hot air]. The cross-linkers are added together with the binder in the print paste formulation with a suitable catalyst [11].

Nowadays the traditional binders used in textile printing are self-cross linking polymers which reticulate during the fixation step. They are supplied as aqueous polymer dispersions, based mainly on acrylate and less commonly on butadiene and vinyl acetate, with solid contents of the range 40-50%. The amount of binder used depends on the amount of pigment and textile substrates, and usually varies within the range 50-150 gm per Kg of printing paste. The surface active substances needed to produce a stable dispersion are responsible for the compatibility of the binder with the other components of the print paste. The fastness i.e. the resistance of the binder film to mechanical stress and its swelling tendency in water and organic solvents must be increased to an acceptable level by the cross linking reaction of the binder. Three dimensional cross-linking of the binder film can be achieved by acid catalysis under usual condensation conditions.

Binder films based on butadiene can age by the action of light and oxygen, i.e. they can become yellow, and their fastness properties can deteriorate. Butadiene binders are therefore not recommended for pigment printed textiles that are continuously exposed to light [11].

Acrylonitrile Based Binders

Pigment print systems include thickeners, binders, cross linking agents and additives such as softeners, humectants, emulsifiers and antifoams. While most of these traditional components may affect the final fabric hand and fastness, the most important component which affects the fabric hand is the binder system.

Acrylic binders, butadiene SBR and their mixture combinations have been known for a while. Acrylic emulsions are expected to resist yellowing upon exposure to light, heat, and cyclically ageing with oxides of nitrogen. They usually are attractively priced. However, they render a fairly harsh hand especially at high concentrations in the print paste. Recent developments in acrylic emulsion chemistry have rendered printing binders with a much softer hand, yet maintaining reasonable price levels and fastness.

Butadiene SBR emulsions provide a softer handle, but they are susceptible to yellowing. Mixtures of both acrylic and butadiene SBR types have been common in many pigment printing formulations [11].

Acrylonitrile-based polymers were a more recent development. The original film produced with acrylonitrile was tough and fairly rigid and was softened with the aid of selected plasticizer. The resultant emulsions rendered excellent printability and fastness to dry crock, dry cleaning and wash. The wet crock fastness properties were good but needed improvement.

Modified versions of the acrylonitrile latex were then developed by adding

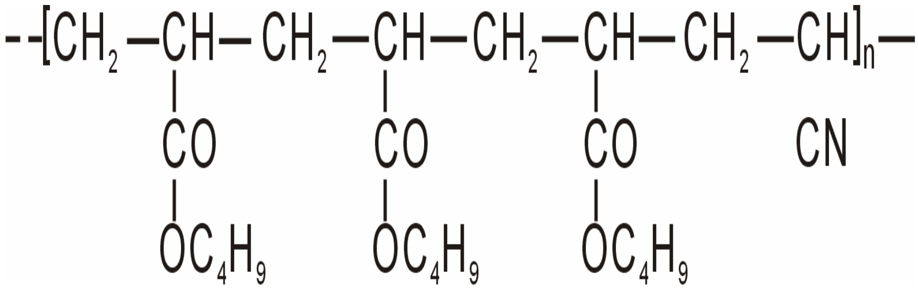

Figure 1. General structure of acrylate copolymer.

special modifying components. These specialty components contributed to an improved wet crock fastness and hand. SUPERPRINT is a specialty latex based on this chemistry [36].

Pigment printing requires higher additions of binders for deep shades. Higher amounts of binder are expected to improve fastness results, particularly to crock and wash. However, the amounts of binder usually level-off at 18-20% in print paste formulations for deep shades, particularly due to a resulting harsh hand.

The most important feature of the latter type of the modified acrylonitrile binders, i.e. SUPERPRINT is that the addition of higher amounts of binder to the print formulation, as required for deep shades, does not adversely affect fabric hand. It is therefore possible to arrive at higher pigment print fastness results by increasing the amounts of the SUPERPRINT binder in the print system without materially affecting fabric hand [11,36].

Soybean Alkyd Binders

The traditional binders used in pigment printing which are based on acrylic resins are obtained primarily from petrochemical raw materials. Alkyd resins made from soybean oil represent a major use of this in agricultural commodity. Utilizing resins and polymeric materials, such as alkyds, made from agricultural derivatives and byproducts will decrease dependence on petrochemicals and increase the commercial benefits for farmers. Alkyd resins are fatty acid modified polyester resins formed by the reaction between a dibasic acid and a polyhydric alcohol, which is then modified with a triglyceride (soybean oil).

A comprehensive study was completed on the potential use of commercial available, water reducible soybean-based alkyd resins for pigment printing 100% cotton and 65/35% polyester/cotton blend poplins. Various printing trials were performed to determine the influence of curing conditions and selected products (catalysts, softeners, low crock agents, and plasticizers) on the quality of the prints. The pigment prints containing the alkyd binders also were compared with fabrics printed with commercial ready-for-use print pastes. All of the print pastes contained C.I. Pigment Blue 15:3 – a widely used phthalocyanine pigment. The quality of the prints was evaluated for color yield, stiffness, and colorfastness properties [11,36].

Chitosan as combined Binder and Thickener

Binders made of natural wood resin, wax, stand linseed or safflower oils and chitosan were tested in order to obtain biodegradable printing paste. Promising results were reported. Among these is the use of chitosan as combined binder and thickener.

The use of chitosan as a combined binder and thickener in pigment printing has been examined in comparison with a commercial printing system (Alco print). Printing pastes made up from mixtures of chitosan, pigment and acetic acid at the appropriate viscosity gave satisfactory prints on polyester and 67:33 polyester/cotton woven fabrics. Rheological data showed the chitosan pigment paste had a much lower yield point than commercial printing paste though no difficulties were found in its use. Curing of the chitosan print at 150 °C for 6 min gave samples of comparable color fastness to the commercial printed samples when subjected to the rubbing and washing tests. The only drawbacks noted in using chitosan in this way were a reduced color yield and much higher fabric stiffness. Using chitosan as binder, no solvent is further necessary [11,36].

Action of binder in pigment fixation

The difference between dyeing processes and pigmentation is that pigment colored textiles require a curing procedure. Since pigments do not have an affinity to textiles. Pigment fixation on textiles relies on binders that require a curing process to hold the pigments on a textile. Conventional curing is a thermal process where pigment colored textiles must be dried and then cured with heat to convert the soft organic base (monomer and/or oligomer) to a tough polymer [37].

UV curing is an alternative to the thermal process. UV curing resin formulations content oligomers, monomers, and photo initiators. These components can be polymerized (hardened) by the free radical mechanism [37-39] shown in Figure 2 using of a photo initiator triggers a nearly instantaneous curing reaction upon exposure to UV light. Thus UV curing produces a completely polymerized network in seconds and is faster than thermal curing [40]. UV curing for pigment printing has been studied [31,41], Problems associated with the process include low crock fastness, stiff fabric hand and low curing efficiency of the resin when pigments are involved. (Figures 2 & 3)

Printing with pigment dispersed in radiation curable liquid compositions and curing with ultraviolet eliminates the drying step and greatly reduces the energy required for curing. High curing speeds, high cross-linking densities and the absence of organic solvents have made UV curing a well-established technology for all kinds of coating and ink applications [4,15,23,41].

Today numerous UV-curable monomers and oligomers like polyether, polyester, epoxy, polyacrylate and urethane acrylates are available. By the choice of raw materials namely oligomers as binders and accompanying monomers, and photo initiators the film properties such as hardness, flexibility, resistance and adhesion can be controlled in a very flexible way [23].

The fastness properties of the prints depend on the type of binder used as well as the type of the selected textile fabric. Both concentration and type of the binders affect the color strength of the UV cured prints [27].

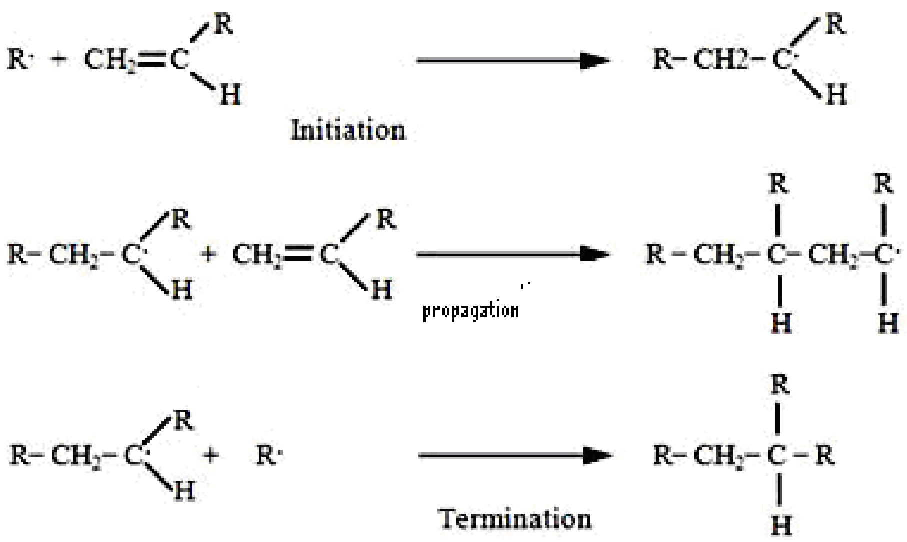

Figure 2. Mechanism of radical polymerization.

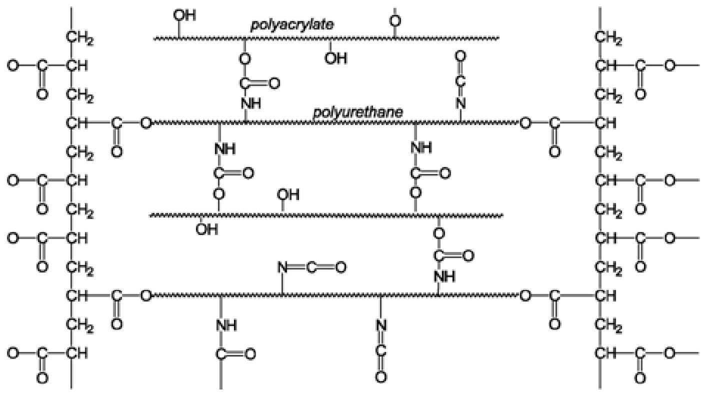

Figure 3. Cross-linked polymer network.

Conclusion

This review paper summarizes that binder are required in pigment printing to bind the pigment onto the textile fibers. In pigment printing, insoluble pigments, which have no affinity for the fiber and fixed on to the textile with binding agents in the pattern required. Binders and fixers play an important role in pigment printing achieving optimum fastness properties. Binders should form flexible films that encapsulate pigment particles and adhere to fabrics without swelling during laundering and dry cleaning.

The binder used in the pigment printing process is usually based on styrene-butadiene, styrene acrylate or vinyl acetate-acrylate co-polymer. Binders are the mechanism used to keep the color on the fabric when using pigments for printing textiles. Different binders were also developed for the purpose of printing and other functions, resulting finally in the use of water- in-oil, and oil-in-water emulsions. This greatly accelerated the use of pigments in textile printing and then pigments have become major coloring matters used in printings. Pigment fixation on textiles relies on binders that require a curing process to hold the pigments on a textile.The fastness properties of the prints depend on the type of binder used as well as the type of the selected textile fabric. Both concentration and type of the bindersaffect the color strength of the UV cured prints.The quality of the prints was evaluated for color yield, stiffness, and colorfastness properties.

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