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Pigment Ink Formulation, Tests and Test Methods for Pigmented Textile Inks

Muhammad Rafique Khan
College of Textiles & Clothing Jiangnan University, Wuxi, Jiangsu, China

Abstract
Cotton, polyester, and cotton polyester blended woven fabrics were printed using an ink jet print using by means of a prepared pigment ink. Literature indicated that the development of insoluble pigment-based inks presents enormous challenges to the ink formulator. Meanwhile, pigments face several application problems in terms of their dispersion stability within the ink formulation, and consequently blocking the nozzles within the inkjet print head.The study was done on route bases: Formation of pigment ink for textile, Tests and test methods for pigmented textile inks, Limitations and Approaches in Development of Pigment Based Inks
Keywords: Binder system, Dispersing agent, Tests and test methods, Ink formulation, pre-and post-treatments.

1. Introduction

In conventional textile screen-printing the use of pigments is the major coloration method, with approximately 50% of the world textile printing market using this method. With improvements in the technology and increasing environmental pressure on dye-based textile printing systems, that require a washing off stage, the use of textile pigment printing will increase further (1).

The developments in conventional textile screen-printing in the coming years will focus on both the physical form of the pigment dispersion formulations and the textile binder and the important chemical components of the textile screen paste formulation. This will produce further improvements in the fastness and handle of the pigmented printed textile. This performance level must also be matched by any textile prints produced by ink jet printing if we are to see increased market penetration of digital textile ink jet printing.

The current textile ink jet printing market is still extremely small and amounts to no more than one percent of the total textile printing market. In recent years, inkjet printing has found an increasing application in textile printing. It has shown considerable benefits in terms of strike-off, preparation of samples such as the flag/banner market, sportswear and niche printed fashion articles and recently in the production of short print-length textile. It is expected that, with further advances in software, printer and ink technologies, the inkjet printing of textiles will increase in importance in future (2).

Unlike printing on paper, in digital textile printing, pretreatment and post-treatment are required to fix the colourants onto the fabrics and yield improves colour appearance and durability. Pretreatment chemicals cannot be included in the ink formulation because they affect the physical properties (such as viscosity) of the ink making it unsuitable for jetting from the print head. The post-treatment processes affect dynamically colour appearance and change the fabric properties (3).

The development of insoluble pigment-based inks and of sparingly soluble disperse dye-based inks presents different challenges to the ink formulator. Different properties are required for specific print based technologies. A particular difficulty is the production of sub-micron milled dispersion inks if adequate stability is to be maintained with pigment-based inks. There are other considerations, because the pigment ink composition is dependent upon the print head technology used in particular, the pigment must be bound to the textile fabric surface using a binder.

In screen printing, the binder is put into the print paste, but in inkjet printing the binder could be supplied as follows:

1) A pre and/or post treatment to achieve the pigment fastness.
2) Develop pigment inkjet inks with textile binder included for specific piezo print head.
3) Develop a new chemical approach for textile inkjet printing using pigment based inks which allows the low viscosity requirement to be achieved without the use of textile binders (4).

2. Formation of pigment ink for textile

The ingredient selection for a typical pigment ink formulation for ink jet digital textile printing includes (5):

- A pigment dispersion for color
- A polymeric binder, a solution polymer or latex for image durability
- Water, for aqueous inkjet inks ± a medium to carry other components
- A co-solvent, helping water to carry other ingredients through solubility and compatibility and enhancing the performance of other ingredients in terms of wetting and adhesion to the substrates and jetting properties
- Surfactants, for nozzle and substrate wetting and jetting reliability and also for stabilizing the key

ingredients such as binder and pigment particles from coagulation

- Humectants, to prevent drying when not printing
- An antifoam agent to reduce foaming
- A viscosity control agent for damping control and droplet formation
- A penetrant to speed drying on porous media such as paper and textile
- A biocide to prevent spoilage.

Aqueous pigmented ink jet inks have existed for some time. But the challenge for textile printing is to incorporate enough binder in the ink for wash ability and at the same time to maintain low viscosity, ink stability and jett ability. To maintain low viscosity, ink stability and reliable jetting, solids level and formulation space are limited. It is important and sometimes critical for an ingredient to serve multiple functions. For example, a nonionic surfactant of long chain polyethylene glycol with a hydrophobe serves as a surfactant to aid stability and to control wetting and surface tension, as humectant to slow water evaporation and therefore preventing the ink drying near the nozzle, and as a rheology modifier to control the viscosity profile and therefore jetting and drop formation. A cross-linkable and ink medium soluble but water insoluble polymer could serve as a dispersant to disperse the pigment, as a binder to bind the pigment particles to the fabric for wash and rub resistance, and as a rheology modifier and possibly as a humectants. The key ingredient selection, their functions and interaction and synergy, will be discussed in detail in the following sub-sections.

2.1 Pigment dispersion selection

Pigment dispersion is probably the most important ingredient, and the rest of the ingredients in the ink jet textile ink formulation either serve to position the pigment particles to the right place on the substrate through a given print head in order to generate beautiful images, or to bind the pigment particles to the substrate so that the image can last a long time with respect to different types of resistance such wash and rub.

The pigment and the set of pigments selected determine the color gamut, the color density, the brightness and the UV resistance of the individual ink and the ink set. These properties are not unique to ink jet and are similar to conventional printing inks, so they will not be discussed further here.

The unique properties which are important in pigment dispersion selection for ink jet inks are stability in terms of the formulated inks, particle size and size distribution, viscosity, surface tension and pigment solids.

The stability of the pigment dispersion with respect to a variety of formula- tion ingredients, solvents, low surface tension surfactants and polymeric binders is very important because if the ink is not stable, the other properties become meaningless.

The particle size and size distribution, on the one hand, affects the image quality, especially color density, in terms of ink holdout and the effective use of each pigment particle for light absorption. Bigger particles are probably good for holdout, leading to higher color density, while smaller particles are probably better in terms of the effective use of each pigment particle for light absorption. When there are competing factors, optimum particle size exists for a given substrate. Although it is not relevant for textile printing, smaller particles tend to yield better gloss for glossy substrates. On the other hand, the particle size and size distribution have a lot to do with settling of the pigment in the ink, colloidal stability, and clogging of the nozzle and therefore the jetting reliability. If the particle size is too big or the distribution is too broad, it will have an adverse effect in start-up and reliable jetting due to settling and clogging. Too many small particles (below 0.05 microns) can also have adverse effects in terms of stability and jetting reliability, because smaller particles have higher surface area to volume ratio, and therefore higher dispersant demand, and at the same time the surface area per particle is smaller, therefore if the zeta potential or charge density is the same, smaller particles have less total charge per particle and the repulsive barrier is lower than that of big particles and in turn may be less stable. Small particles may also provide high probability for clogging due to particle congestion.

Typically pigment dispersions with low viscosity and high surface tension are more preferable. Low viscosity in pigment dispersion means leaving more room for other ingredients such as polymeric binders and greater ease in maintaining overall viscosity of the final inks . If the surface tension of pigment dispersions is high, there are always ways to lower the surface tension of water-based systems by adding surfactants and organic solvents. On the other hand, if it is low, it will put a limit on the surface tension of the final ink.

Finally the solid level is a very important concern. Typically higher is better, because it leaves more room and flexibility for adding other ingredients to the ink formulation without compromising the pigment solids loading in the final ink: 10% is at the lower end of most pigment dispersion suppliers, 30 to 40% is at the high end and 20% is typical.

There are two major types of pigment dispersion, polymeric dispersant stabilized dispersions and self-dispersed dispersions. The type is not important as long as they provide the right properties outlined above. The self-dispersed type tends to be more stable with respect to solvent selection, while polymeric dispersant stabilized dispersions tend to have better permanence, such smear resistance benefited from the polymeric dispersant. Some of the key pigment dispersion suppliers are Rohm and Haas, Lanxess, Clariant, and Cabot. This is by no means a complete list.

2.2 Binder selection

While pigment is an important ingredient to provide the image, the binder is another key ingredient to maintain the permanence of the image with respect to washing and rubbing in the case of textile printing. Incorporating polymeric binders in ink jet inks is difficult in general. It is even more difficult for textiles because it requires not only high levels but also low transition temperature (Tg) for good hand and feel. The following example will help to illuminate the difficulty. Most people have the experience of using Elmer's™ glue, which is a soft and low transition temperature (Tg) polymeric binder. How often we need to cut the tip in order to remedy the clogging to use it again and it has only one big nozzle. The specific challenges are

- To keep the soft and low Tg binder from clogging the nozzles.
- To maintain the low viscosity and formulation space for jetting reliability and at the same time to load enough binder for wash and crock resistance, especially for low viscosity print heads.
- To achieve adequate (1 to 2 years) stability and shelf lifetime with regard to sedimentation, homo- and hetero-coagulation and phase separation.

To overcome these difficulties, leading companies in this field have developed proprietary polymer and formulation technology, which may include ink medium soluble, but water insoluble random or block copolymers with or without cross-linking functionality, dispersants, binders and other property combined cross-linkable multi-functional agents and protected cross-linkable latex polymers. For example, in the case of protected latex polymers, the soft and sticky binders are protected by a thin layer of shell, like an egg; it is not sticky in the ink before the protective shell is broken, and becomes sticky glue only when the protective shell is broken in the later curing stage.

2.3 Co-solvent and humectants

Pigment is the important ingredient to provide the image, and binder is the key ingredient to maintain the permanence of the image. But both need a carrier to deliver them to the substrate. In the case of water-based pigment textile inks, the carrier is mainly water (50 to 80%) mixed with water-soluble organic com- pounds, which are called co-solvents and humectants based on their functions.

Co-solvents are organic compounds such as 2-pyrrolidone and propandiols, which help water to incorporate other ingredients into the system better. For example, 2-pyrrolidone may help water to dissolve some surfactants better and to make some polymers more soluble. Humectants are hydroscopic organic compounds such as polyethylene or propylene glycols with or without alkyd ether capping groups on one or both ends, glycerol, sorbitols, etc. Hydroscopic means capable of `pulling' water vapor from the air back to the liquid phase, which slows down or completely stops the drying of the ink when humectants reach a certain concentration under a given humidity and temperature condition. This is very important to prevent the ink from drying on the nozzle and from clogging the nozzle both during the printing and in the idling state. A single ingredient or compound, for example, 2-pyrrolidone, often serves as both co- solvent and humectant.

2.4 Surfactant selection

Surfactants are another key ingredient in terms of delivering the pigment and the binder from the ink to the substrate through the print head. High HLB (hydrophilic and lipophilic balance) surfactants are used typically for aiding the colloidal stability of the systems, and low HLB surfactants are used to lower the surface tension, so the ink can wet the nozzle capillary to establish and maintain the meniscus at the nozzle tip. The importance of maintaining the meniscus at the nozzle tip both in the steady state and in the dynamic state during jetting cannot be overemphasized because it is so critical for start-up, reducing latency (defined as number of firings needed before the ink establishes the first stable drop of jetting), increasing the elapsed time between jetting without refreshing and ultimately long-term reliable continuous printing. For some print heads, reliable jetting or printing can be achieved even when the nozzle plate is wetted. This low HLB surfactant is also a major factor which determines the interaction between the ink and the substrate and therefore controls or affects wetting, bleeding, dot-gain, dot-quality and ultimately the image quality. Surfactants affect these properties through a physical parameter, namely surface tension (both static and dynamic). The most popular surfactants used for this purpose are relatively short-chain ethylene glycol nonionic surfactants such as the Air Products Surfynol™ line of products like Surfynol™ 465. Anionic surfactants such as Aerosol™ OT are also used.

2.5 Rheology modifier selection

While a surfactant is the key ingredient used to control surface tension, a rheology modifier is the ingredient used to control the viscosity of the ink, or more precisely the rheology profile of the ink, which includes the yield stress and the viscosity at different shear modes and rates. The yield stress along with the meniscus has a major effect on the latency. The viscosity at low shear rate along with the surface tension determines the fill-up and the priming of the nozzles to establish the initial meniscus and the ready-to-jet condition. The viscosity at high shear rate, up to 1 million reciprocal seconds, is probably more relevant to fluid dynamics and the drop formation at the nozzle tip and thereafter. The viscosity and the mass density of the ink affect the oscillation and the damping of the ink chamber and therefore the jetting. Water-soluble polymers such as polyethylene glycols (PEG) with molecular weight ranging from several hundred up to hundreds of thousands could be rheology modifiers. The rheology modifiers along with the co-solvents, humectants and the total solids in the case of pigmented inks with or without binders together determine the viscosity. Ideally the rheology modifier is selected with the following considerations in mind.

1) It should not strongly associate with multiple pigment and/or latex particles, causing coagulation and precipitation, unless the coagulation is well controlled.
2) Associative thickening should be avoided since even loose association through the rheology modifier molecule may increase yield stress and cause phase separation.
3) Depletion flocculation should also be avoided because it may cause phase separation and non-uniform color density in the print.

In case 2, the rheology modifier molecule will be more likely in the particle rich phase, while in case 3 the opposite applies in that the rheology modifier molecule will be more likely in the particle deficient phase. In general, the viscosity of ink jet ink is low, below 20 cps. Even at this low viscosity, the rheology profile cannot be overlooked and it may be important that it is controlled intentionally with relatively high molecular weight water-soluble polymers.

2.6 Other miscellaneous ingredients selection

Pigments, along with dispersants, binders, co-solvents, humectants, surfactants and rheology modifiers (viscosity adjusters), are the main functional ingredients of pigment ink jet ink formulation for textile printing. Other ingredients such as de-foamers, penetrants and biocides may be added as needed. The defoamer is for defoaming as its name suggests. The penetrant helps the ink vehicle to be absorbed into the substrate faster and therefore may make the print touchable sooner. Biocide is for preventing bacteria growth and maintaining ink shelf lifetime. It is always a good rule to keep the formulation simple; if not needed, do not put it in or take it out. When possible, use one ingredient to serve multiple functions.

2.7 Putting them together ± synergies among all the ingredients

As stated in the previous sections, pigment is to provide the image, binder is to keep the image permanent, water along with co-solvents is the vehicle to carry the pigment and binder, and surfactants and rheology modifiers are to provide the right surface tension and rheology for reliable jetting through the nozzle and for the proper interaction with the substrate to create a high quality image. Each ingredient needs to do its own job and at the same time to work together in harmony.

If the binder is polymeric latex particles, the binder particles and pigment particles need to have the right energy balance so that they will not be so attractive to each other to create stability problems and at the same time they should not repulse each other in a way to create pigment and latex particle phase separation. Co-solvents such as 2-pyrrolidone along with water are not only a carrier for pigments and binders, but also help to dissolve the low HLB surfactant to make it more effective and to transport it quickly through the medium to ensure low dynamic surface tension. Co-solvents and low HLB surfactants work together to create better wetting condition for both the nozzle and the substrate . Co-solvents often soften the binder and substrate to enhance adhesion. Long EO chain high HLB surfactants can serve as stabilizers, humectants and also rheology modifiers. They can also emulsify the low HLB surfactant to prevent it from forming an oily layer on top. The low and high HLB surfactants together with the co-solvent may form a good cleaning solution for metal and semiconductor surfaces, so the ink is self-cleaning. Polyethylene glycols (PEG) serve as both humectants and rheology modifiers.

3. Tests and test methods for pigmented textile inks

As in any field, in aqueous pigment ink jet textile ink formulation, knowing the ingredients and their functions is not enough; we also need to know the important properties and how to test these properties.
The following 22 properties/test methods are important in developing pigmented textile ink jet inks.

1. Viscosity
2. Surface tension
3. PH
4. Particle size (PS) and PS distribution
5. Total solids
6. Ink mass density
7. Ink filterability
8. Foaming

9. Air content in the ink and degassing.
10. Drying rate at controlled temperature and humidity and re-dispersability
11. Heat-aging stability (3 days, 10 days and 28 days by PS, ST, viscosity, pH,total solid at 60C)
12. Settling rate at regular or accelerated gravity
13. Phase separation
14. Ink fill-up
15. Continuous jetting reliability (x number of square meters of continuous printing without defect)
16. OD or color density
17. L.a.b.
18. Printability (resolution, inter-color bleeding, and color uniformity)
19. 3A wash fastness
20. Dry and wet crocks
21. Dry cleaning fastness
22. Regulatory and safety (wet ink and dry printed sample).

These 22 properties and test methods are separated into seven groups, which consist of a basic property group (1 to 6), a jetting reliability property group (7 to 10), a shelf lifetime property group (11 to 13), actual jetting reliability tests (14 and 15), an image quality related property group (16 to 18), an image permanence property group (19 to 21) and a regulatory and safety group (22).

3.1 Basic physical properties

The first six properties (1 to 6) are the basic physical properties. The required value may be unique, but the properties themselves are not. These properties, especially the first three, are specified for a given design of print head. The viscosity (or more precisely the rheology) determines the fluid dynamics for the specific design of the print head geometry, e.g. the sufficient supply of the ink for starting the jetting and during jetting and the drop formation. Otherwise, Start-up, latency and ink-starvation massive nozzle dropout can occur. The simple low shear rate Brookfield^{TM} viscosity is far from enough to know the rheology profile of the ink. Even if the rheology profile is known, it is still difficult to predict the fluid dynamics and drop formation due to the complicated geometry of the ink pathway and the driving waveform. One thing print head manufacturers have done is to do computer-based simulations using finite element analysis methods. Nonetheless, the simple Brookfield viscosity provides a starting point and gives the formulators something to think about.

The optimum surface tension for jetting is determined by the surface energy of the channel of the nozzles vs. that of the front face of the print head in such a way that the ink does not ooze out and wet or dirty the front face, but has the maximum force to wet the channel to maintain the proper meniscus at the orifice of the nozzle. The proper meniscus at the orifice of the nozzle must be maintained both when it starts to jet and during the jetting, which means both the static and dynamic meniscus needs to be right. This requires both static and dynamic surface tension to be right. Again the simple static surface tension only provides a starting point and gives the formulators something to think about. In some situations, stable jetting can be achieved even when the front face is maintained wet during jetting. In this case, the ink has to be slow-drying; otherwise nozzle clogging or partial clogging could be a major issue. It is also important to understand that even when the static surface tension of the ink is lower than the surface energy for the front face of the nozzle, the front face may not be wet during the jetting because the dynamic surface tension may be higher than the surface energy of the front face. The optimum surface tension for jetting is not likely to be the optimum surface tension for wetting or controlling the bleeding or coalescence on the substrate of interest. Compromise is unavoidable.

The pH and other chemical characteristics of the ink are important in terms of its compatibility with the construction materials of the print head. The compatibility means that the ink should damage neither the print head materials nor the adhesive bond between different head parts and also that the print head materials should not leach out any material to change the ink composition or properties in any way affecting the stability, jetting or ink performance on the substrate. The particle size and distribution, total solids and mass density of the ink are properties affecting jetting in very subtle ways.

3.2 Ink and print head interaction properties

Beside the chemical compatibility between ink and print head mentioned in the previous section, the next four properties (7 to 10) are particularly important in terms of jetting reliability, especially for piezo-based print heads. The ink flow from the ink supply to the substrate during the ink jet jetting process is indeed a series of filtering processes through very small (micron size) orifices such as filters in the damper and the nozzles themselves at very high shear rate (~1 million s 1). The filterability is related to both the content of large particles and shear stability to some degree. It is highly important in ink jet inks because it could shorten the lifetime of the print head. The air content can be measured using an oxygen meter. Typical water contains about 7±8mg oxygen per gram or 7±8ppm. For piezo print head, less than 4mg/g or ppm may be desirable. This is because the high air content in the ink (foam or dissolved) makes the compressibility of the ink high, and when the compressibility is high, the periodically pulsed jetting force or energy is converted to thermal energy and is wasted, instead of being used for ejecting the ink drop. This is particularly important for piezo heads because the jetting push for piezo is relatively high force, short duration and low volume capacity. When the bubbles are big (foam), they could clog the nozzles for both piezo and thermal print heads. Both chemical and mechanical methods of defoaming and degassing have been used.

The drying rate at a given temperature and humidity determines the idle time and the continuous jetting reliability at that temperature and humidity due to crusting, and these problems magnify when the front face gets dirty due to oozing, misting and filament springback due to poor drop formation. The re-dispersability of the ink also determines how easily the `spitting' and `wiping' of the maintenance cycles can recover the problem.

3.3 Shelf lifetime properties and actual jetting reliability tests

Properties 11 to 13 determine the shelf lifetime of the ink. The heat-aging stability test is an accelerated test, which measures basic ink properties at different time intervals at 60C heat aging. One week of heat aging is approximately equivalent to three months at room temperature (20±25C), and four weeks is approximately equivalent to one year. The test can and should be extended to all other properties at the desired final heat-aging time interval before commercialization. Settling rate at regular or accelerated gravity and phase separation are two other properties which are very important in determining shelf life time, especially for polymeric binder containing pigment ink jet inks.

Properties 14 and 15 put properties 1 through 10 into real jetting tests. Test 14 is about how easily one can get the print going perfectly when a new set of ink cartridges is installed, while test 15 is about how long the reliable jetting can last once the printing gets going. Tests 14 and 15 can be performed on cheap paper substrates. They do not need the right textile substrate because they only test how well the ink interacts with the printer in terms of jetting reliability. In the next section, we will discuss how well the ink interacts with the intended textile substrate in terms of printing quality.

3.4 Ink and media interaction properties and image quality

Properties 16 to 18 are about how the ink interacts with the substrate and the image quality for the textile substrate of interest. Optical density (OD) for black, and color density for cyan, magenta, and yellow, are used to assess the intensity that each process color ink can offer, while the L.a.b. measurements provide the full color space (gamut) which a given set of process color inks can achieve for a given printer, printing mode, software and substrate combination. The color density and gamut information is typically stored in a file called the color profile for the given combination. The color intensity and color gamut along with resolution (how fine a line can be printed), inter-color bleeding (how sharp the interface can be between two colors) and color uniformity determine the image quality and the printability. These properties are obtained through spectra colorimeters and image analysis software. To obtain a high quality image is the first step while making the image durable and permanent is the next key step in digital textile printing.

3.5 Durability and permanence of printed images

Durability and permanence of the printed images are the key for a successful set of pigment inks for inkjet textile printing. Unlike the reactive, acid and dispersed dyes, the pigmented inks rely on external polymeric binders to achieve the durability and permanence of the printed images. The polymeric binders provide the permanence properties through mechanical binding of film formation and chemical interaction and cross-linking with the substrate. The mechanical binding works for all fiber types of textile substrates; cotton, polyester, cotton and poly blend, and silk to name a few. But chemical interaction and cross- linking only occur when the polymer and the fiber of the substrate have the right pair of chemical reaction functional groups. Therefore, people claim the binder-containing pigment inks work for all fiber types due to the mechanical binding and work best when there is chemical cross-linking between the polymer and the fiber. The hydroxyl group on the cotton fiber is one of the best examples.

Both mechanical binding and chemical cross-linking require the printed samples to be heated. The heating temperature and time depend on the glass transition temperature (Tg) for the mechanical binding and the chemical reaction rate for the cross-linking, which typically ranges from 100C to 200C and from 30 seconds to 5 minutes. Two types of heating devices are used for the image fixation: heat presses and hot air ovens. The heat transfer of hot air ovens is through air flow while the heat press is by contact, so the hot air oven takes longer and/or needs a higher temperature than the heat press to reach the same curing point. In the case of a heat press, not only the time and temperature but also the pressure is very important to determine the cure and the fixation for wash and rub, because higher pressure means better heat transfer. The cure conditions need to be optimized for each ink set and fabric combination to achieve the best possible permanence properties without damaging the fabrics. After proper curing and fixation, water and detergent wash fastness, wet and dry crocks or rubs and dry cleaning fastness tests

(19 to 21) can be performed, based on standard test methods from the Technical Manual of the American Association of Textile Chemists and Colorists, in the same way as for conventional screen pigment printing.

3.6 Regulatory and safety considerations

Although regulatory and safety considerations are beyond the scope of this chapter, their importance should not be overlooked. Both the wet ink and the dried print samples need to be safe for handling and wearing or use. Before commercialization, the safety and regulation of both the ink and printed samples should be assessed by the right professionals.

4. Optional pre-and post-treatments for pigmented digital textile printing

The pre-treatment for pigment printing is optional and the post-treatment is simple: dry heat. For pigment digital textile printing, due to limited formulation space and low viscosity, the pigment, binder and other ingredients loading are limited, so pre-treatment with polymers, cationic materials, catalysts, reactive cross-linking agents, etc., may be needed in some applications to enhance color density, image quality, durability and permanence of the image. Spray or screen print polymer binders over the printed images may be a necessary post-treatment for difficult substrates or applications which require extra durability.

5. Why Develop Pigment Based Inks?

Different textile substrates have different colourant requirements due to the difference in the mode of colour-substrate interaction. This is shown in Table 1.

Table 1 Selection of colourant for textile substrates and their mode of interaction with fibres (6)

Colourant	Fibre	Colour- Fibre Interaction
Pigment	All fibres	No interaction – complex surface polymer bonding mechanism
Reactive dye	Cotton, Silk and Wool	Covalent fibre bonding
Disperse dye	Polyester	Hydrophobic- Solid State Mechanism
Acid dye	Silk, Wool and Nylon	Electrostatic and Hydrogen bonding with fibre

A single set of inks which can be used to print most of the textile substrates, especially blend fabrics will have benefits such as lower production costs, better productivity, improved colour prediction and reproducibility and low effluent. One approach that has been undertaken by researchers was to develop a universal set of dye based inks which can enable ink jet printing on chemically diverse textile materials (7). Another approach has been to develop pigment based inks as pigments are substrate independent and can be applied on most textile materials. Pigments appear to be the most suitable candidates to achieve the above mentioned benefits. With increasing environmental pressure on dye based colourant systems and with improvements in pigment applications, it is expected that there will be a rapid growth in pigment based colourant systems. In 2002, out of 24 billion square metres of fabric printed worldwide, 48% was done using pigment as the colour source. A recent study by BASF predicted that textile printing using pigments will increase from 11 billion square metres in 2002 to 15 billion square metres in 2012 (8). Thus, developing pigment based inks and fixation processes will have advantages of conventional pigment printing such as ease of application, simple fixation via curing and elimination of costly washing and steaming processes. The efficiency and economy of ink jet printing of textiles can be greatly improved using pigment based inks and processes for their fixation.

6. Limitations and Approaches in Development of Pigment Based Inks

Developing pigment based inks still presents a range of limitations with respect to particle size requirement, dispersion stability and the requirement of a binder. The effect of pigment binder on fabric handle is a major issue compared with dye based inks. Moreover, inks based on pearlescent, metallic and white inorganic pigments are still not available (9).

6.1 Particle Size

The particle size of the pigments for ink jet printers should be well below one micron in order to prevent the clogging of the fine jet nozzles. Also, in order to be comparable to dyes in colour vividness, the mean particle size should be around 100 nm. Recent developments in nanotechnology have allowed successful preparations of various dispersed pigment nanoparticle systems through a milling process (10-11).

6.2 Dispersion Stability

Pigments are insoluble in water and therefore do not dissolve as individual molecules but take the particulate form. Due to this, they form aggregates over a period of time leading to crystal growth which is main cause of clogging of the nozzles. Hence, stabilisation of pigment dispersions is a critical issue. Generally, pigments are dispersed in suitable aqueous or non- aqueous solvents. Conventional dispersion technology involves use of various dispersants and surfactants to stabilize pigments. The emerging dispersion technologies are microencapsulation and surface modification.

6.3. Textile Binders for Ink Jet Printing

6.3.1 Binder Requirements

Pigments have very little affinity for textile fibres. This necessitates the use of binders, normally vinyl or acrylic based polymers, for pigment fixation. It is believed that a film is formed by cross-linking of the polymer on the fibres surface thereby entrapping the pigments and hence fixing them onto the fibre surface to achieve acceptable colour fastness (12-13). Textile binders are synthetic polymers based on non renewable petrochemical products. Therefore, there is an incentive to develop binder systems based on natural, renewable resources. Also, for ink jet ink formulations, there is a limit to the amount of binder that can be used due to the viscosity profiles of the print head technology. Possible approaches for developing pigment based inks for most popular print head technologies are shown in Table 2.

Table 2 Matrix of textile pigment ink formulations and print head technologies (8)

Pigment ink	Low viscosity Piezo print-head	High viscosity Piezo print-head	Thermal print-head (Bubble-jet)
With no textile binder	Yes	Yes	Yes
With conventional textile binder	No	Yes	No
with special binder systems	Yes	Yes	No

Low viscosity inks are those inks with viscosity lower than or equal to 5 centipoise while those with viscosity ranging from 10 to 20 cps are high viscosity inks (8). High viscosity inks have been formulated using conventional binders and are available commercially. However, pigment based low viscosity inks are still not available. Conventional textile binders tend to increase viscosity beyond the performance parameters of most of the ink jet printers.

6.3.2 Binder Application

In screen printing, binder is incorporated in the print paste, whereas for ink jet printing, possible approaches are:-

- Application of binder by a post-treatment after ink jet printing
- Incorporation of binder in the ink formulations
- Application of binder by a separate nozzle system (13)

The primary goal was to develop a pigment ink jet printing system which used a natural biopolymer, as the binding system. Two approaches to the application of the natural biopolymer were explored. One was to incorporate the biopolymer into pigment based ink jet ink. The second approach was to develop a two step process where the biopolymer was applied separately as a post-treatment after ink jet printing. Cotton was selected as the preferred substrate as this fibre dominates global printing production.

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ABOUT AUTHOR:

Muhammad Rafique Khan—is currently doing Masters in Textile from College of Textiles & Clothing Jiangnan University, Wuxi, Jiangsu, China He received his BS Textile Degree in 2012 from Indus University, Pakistan.