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THE CHEMISTRY OF INKJET INKS FOR DIGITAL TEXTILE PRINTING - REVIEW

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ABSTRACT

Inkjet inks are the most important component in inkjet printing. The formulation and chemistry of inks determine the printing quality as well as jetting characteristics. Digital printing technology has transformed textiles printing with significant success in terms of print speed, print head technology and color gamut. Nonetheless, ink penetration and its related quality problems are still receiving a high level of attention by researchers around the globe to develop superior inks that can surpass the quality of prints obtained by the conventional methods of printing. This review seeks to take a perfunctory look at the various ink chemistries being developed to address the color related problems in digital textiles inkjet printing and the various pretreatment technologies available for ensuring excellent K/S and color fastness as well as jetting behavior of Newtonian inkjet inks in DOD drop formation. In addition, various issues relating to quality of digital inkjet printer fabrics and ink development have been highlighted. Significant strides have been made in the quest for environmentally friendly universal inks that can print all textiles substrate.

KEYWORDS: Inkjet Ink, Dye, Pigment, Digital Printing, Textile

INTRODUCTION

Inkjet printing has become the new frontier in textile printing, offering advantages in process efficiency, ease of use, cost effectiveness and environmental impact (Pekarovicova 2016a, Magdassi 2010). Digital fabric printing has rapidly evolved over the last few decades creating new opportunities for designers, printers and consumers alike. One important component of this technology besides the machinery is the ink. The study and growth of inks dates back to 2500 B.C. when the Egyptians and Chinese invented carbon residue made from burning oil mixed with water or gum by the first century and used it for various purposes(Dharmesh 2005). Since then there has been slow and steady growth generally in color development. Today, modern ink industries are motivated by constantly changing printing technologies and demands from the printers and end users (Dominioni 2003). Faster printing speeds, more cost-effective processes, and tougher environmental regulations are a few of the challenges currently facing the ink industry (Magdassi 2010).

For all the different types of inks, there are two very important properties thus cohesion and adhesion. Cohesion describes the ink's ability to hold together; adhesion refers to its power to stick to a different material, e.g., a substrate (Adams 2004, Fromm 1984). These two properties are common from the point of view of the physico-chemical nature of the pigment particles especially because their disperse ability is defined by the amount of energy required to distribute the individual pigment particles in a continuous medium so that each pigment particle is completely surrounded by the medium, and no longer makes contact with other pigment particles(Oyarzun 2000). The intra-molecular and intermolecular forces existing within the primary pigment particles within a medium and between pigment particles significantly influence the cohesion and adhesive forces operating between the pigment particles and substrates.

There have been many trendsetters who discovered this process and applied it to a wide variety of inks markets. A number of these pioneers have come from the traditional textile-printing background to learn digital printing, while others have come from the graphics field and are having to learn some of the techniques from the traditional textile industry due to the advancement in development and the ease with the entire printing process.

Ink Jet Ink Applications

One of the most stirring aspects of digital textiles printing is the incredibly wide array of markets in which it can be applied. Hitherto, traditional rotary screen textile printers experimented with applying standard graphics inks to fabric using regular graphics printers in order to develop new patterns without incurring the high costs of rotary screen engraving . Immediately digital inks were produced from textile dyestuffs, many textile printers began to see other benefits over graphic inks. The dyestuffs could be “fixed,” exactly as they would be if rotary printed. (Schindler 2004, Blank 2004). This development led to applications in printing flags, banners and signs, apparel, home furnishings and quilting fabrics, nonwoven and technical textiles, gaming tables, even leather(Tpiller 2005, Schulz 2002). Printers around the world now print all of the materials involved in these markets using digital inks on daily basis. Meanwhile, developments in ink chemistries have now led to three major markets where digital textile printing(Owen 2000). These are sampling, strike-off and mass customization.

Sampling

Initially, the diminution of sampling costs and time played a major role in accommodating digital printing technology for fabrics(Ali 2008). In the textile industry sampling means printing pattern on both paper and fabric with attention to details and in compliance with traditional screen printing (Lin 2004, King 2013, Mills 1994).

Before introducing digital textile printing, sampling was a time and money consuming process, lasting for weeks. With the introduction of digital textile printing the sampling production time has been reduced to few hours(Owen 2000, Tyler 2011).

Strike-Off

Strike-off is a way of producing a sample of a single, salable item for markets such as luxury, entertainment, or special events. Strike-off has also become the second major application area for digital textile printing(Tyler 2011). With high quality digital printing capabilities it is much more economical and time efficient to produce low volume orders by the use of the digital textile printing. Powerful software tools also allows for better control of quality and repeatability of the produced items. To cap it all, the flexibility of the digital textile printing process allows the customer to make modifications to the initial design more easily and prompts for better service solutions that could not be offered rotary or flat bed screen printing companies(Lin 2004).

Mass Customization

Mass customization is the third major application area for digital textile printing. The concept of mass customization was defined by (Hgilmore 1997)"producing goods and services to meet individual customer's needs with near mass production efficiency". It became a new tool in business competition for both manufacturing and service industries. It implies a great increase in variety of goods or services without a corresponding increase in costs. Introduction of digital textile printing allows smaller companies that do not host the industrial fabric printing facilities to offer their services in the field of textile printing(Owen 2000). Considering the fact that the world has become a global village due to the power of the internet, it has become possible to reach customers everywhere around the globe creating totally new business opportunities for the mass markets (Tpiller 2005).

They achieved some level of success much to the chagrin of rotary screen engravers, but this process had some limitations because the traditional graphic inks don't "fix" on textiles, textile dyes became an attractive choice on which to base inks(Provost 2010). Thus, a few dyestuff companies endeavored to develop digital inks from their textile dyestuffs.

Classification of Inkjet Inks

Inkjet inks are generally classified into two broad categories namely 1. Base 2. Colorant. The base refers to the media through which colorant is dissolved or dispersed and applied whiles the colorant refers to the type of colorant being used within the medium thus dissolved dyes eg. Reactive dyes, organic or polymeric dyes or disperse colorant such as pigment and disperse dyes (Le 1998, Cie 2015b, Alexandra Pekarovicova 2016, Niaounakis 2015a, Pekarovicova 2016b). Figure 1 illustrates the classification of inkjet inks.

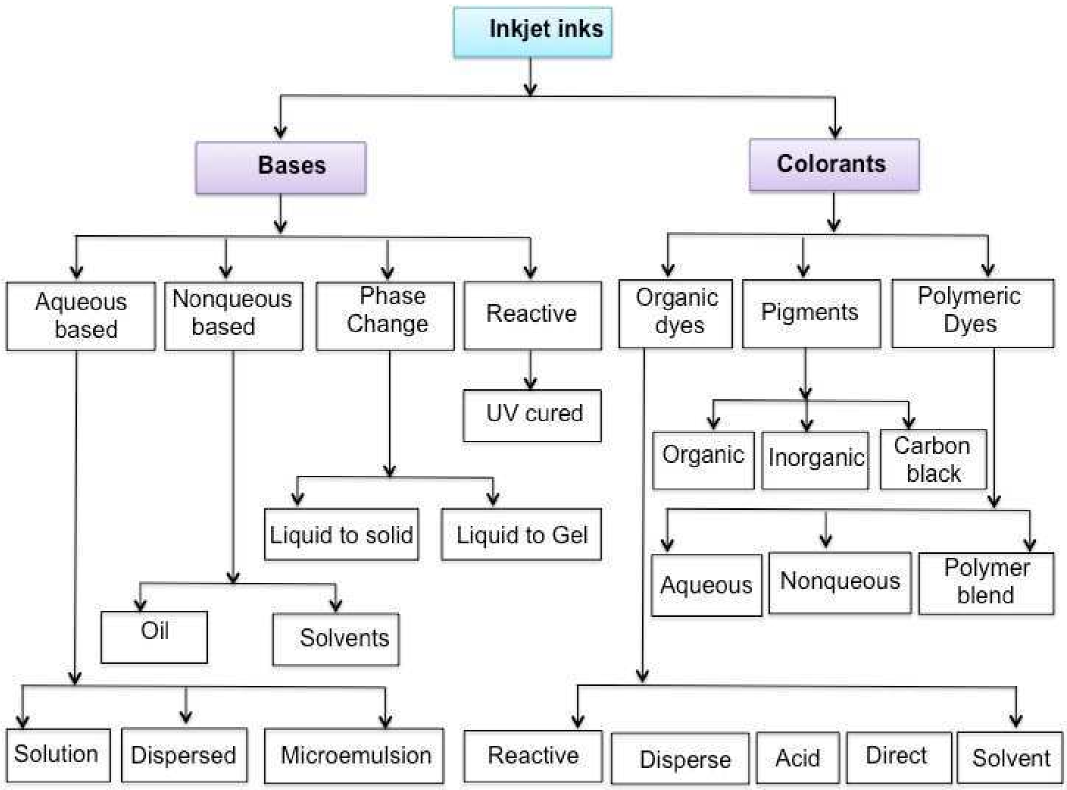


Figure 1: Classification of Inkjet Inks (Le 1998)

The Quest for Cleaner Productions

With the recent quest for cleaner productions, special attention has been paid to inks that eradicate waste, emissions, and reducing energy input in manufacturing and the reduction or eradication of volatile organic compounds (VOCs) from inks have received a major boost (Niaounakis 2015a, Hawkins 2003). So far, water-based inks have proven to be the solution to reducing VOC emissions because these inks are generally cheaper, reduces atmospheric pollution, have less solvents, lowers fire risks, produces less print odor, and are easier to wash-up on printing equipment(Ali 2008). Water-based inks with little or no VOCs have been developed for both thermal and piezoelectric inkjet applications (Yeates 2011, Ujiie 2006). It has been commonly used in home and small office inkjet printers like the Hewlett-Packard Desk Jet series, Canon BJC series, and Epson Color Stylus series. These inks have superior advantages due to less bubble formation, which is common in most thermal inkjet printers for digital textiles printing (Provost 2010, Tyler 2005). Water-based inks are easy to clean from print heads and ensures less nozzle clogging once the rheology of the ink is Newtonian(Xu 2005, Żołek-Tryznowska 2016a). The composition of water-based digital textiles inkjet inks is stoichimetrically formulated to meet specific requirements of substrates. Table 1 shows a typical composition of water-based inkjet ink for printing textiles.

Table 1: General Composition of Water-Based Inkjet Inks(Le 1998)

Component	Function	Concentration (%)
Deionized water	Aqueous carrier medium	60 - 90
Water soluble solvents	Humectants, viscosity controller	5 - 30
Dye or pigment	Provides color (Chromophore)	1-10
Surfactant	Wetting agent, penetrating agent	0.1 - 10
Biocide	Prevents growth of biological organisms	0.05 – 1
Buffer	pH controller	0.1 – 0.5
Other additives	Chelating agent, binder, defoamer etc.	>1

There is no universal stoichiometry for all colorants; the formulation normally varies depending on the specific desire of the chemist. For instance, a study conducted by Wassim Kaimouz 2010 gave a similar formulation to the one by (Le 1998)for bifunctional reactive dye water-based inkjet inks.

Composition of Inkjet Ink Based on Printer

Inkjet inks are the most important component in inkjet printing. The formulation and chemistry of inks determine the printing image quality as well as jetting characteristics of inks and reliability of printing(Yeates 2011, Jackson and Douglasbauer 2005). The content of digital textiles printing vary greatly depending on the type of colorant, the formulation base (water, oil, organic medium), the printing machine to be used, and the mode of curing (Lin 2004).

Table 2: Below Shows a Typical Ink Jet Ink Stoichiometry Based on Type of Printer (Momin 2008)

Ink Component	CIJ CMYK	DOD CMYK
Polymer emulsion	8-14%	8-14%
Water	Balance	Balance
Surfactant	0.05-1%	0.05-1%
Humectants	5-10%	5-10%
Conditioning agent	0.25-0.5%	0.0%
Thickener	0.0%	0.5-5%
Cross-linker	0.5-1%	0.5-1%
Pigment dispersion	2-5%	2.5%
Particle size	1 micron	1micron
Viscosity	3-5cps @ 25^0C	10-14cps @ 25^0C
Surface tension	30-35 dyne/cm	30-35 dyne/cm

Several factors such as base colorant and its content, print head technology, kind of printer (DOD, CIJ) are the major causes of variations in formulation of water-based inkjet inks.

Colorants Contents in Digital Textiles Printing Inkjet Inks

The main function of the ink is to bring a functional molecule, usually a colorant, to a substrate or simply put, to change the color of the substrate (Pekarovicova 2016b, Pekarovicova 2016a). If the colorant is a dye molecule (or combination of various molecules) it should be present at a concentration much below its solubility limit, otherwise slight variations during storage (e.g., temperature, pH) could cause precipitation. In such inks it is essential to determine the dye solubility in presence of all the components, especially at low temperatures. The optical properties of dyes are often affected by slight variations in pH and presence of electrolytes (in water-based inks), medium polarity, and presence of surfactants (possible solubilization) (Cie 2015b, Magdassi 2010). To ensure excellent stability and good consistency, Momin 2008suggested that, dispersed colorants(pigments and disperse dyes) content in inks especially for textiles applications should not exceed 4% by total weight of ink. Others have however recommended that digital textiles inkjet inks in general should have a pigment volume fraction of less than 10% the total weight of the formulation(Pal 2011, Czettlemoyer 1955).

Proper dispersion of pigments in printing inks is important for several reasons but the effect of dispersion quality on the rheological behavior of digital textiles inkjet printing ink is perhaps the most important criterion. Because of the application methods, flow properties are important in digital textile inks; and this is certainly a hurdle that a printing ink must satisfy in order to be considered for potential use (Oyarzun 2000). Therefore, before pigments inks are loaded into a digital textiles inkjet printer, there is the need to kinetically stabilize the ink from flocculation hence its occurrence can have a significant effect on the hue of the printed textiles and cause nozzle clogging of the printer(Niaounakis 2015a). On the other hand, non-graphic inkjet inks, such as conductive or ceramic inks, may contain pigments at concentrations greater than 50%. Oyarzun 2000 indicated that higher pigment loading in inkjet inks could result in poor stabilization which will consequently affect the jetting behavior, print quality and color brightness but may then be case for conductive and ceramic inks because inks for such purposes need high viscosity to be able to thermodynamically remain stable when applied.

In general, dye-containing inks are more stable than inks containing pigments, since the ink is thermodynamically stable (all components are dissolved in one solution), while in pigment inks the system is only kinetically stable (Lin 2004, King 2013).

Conventional UV curable inks usually contains dye or pigment at concentrations below 10% w/w in order to achieve the required optical density which can be made from a blend of monomeric and oligomeric acrylates or epoxies that are polymerized using UV light in the presence of a photo-initiator (Samane 2016). Upon exposure to irradiation, all the ink components are chemically cross-linked; thus the printed film is instantly hardened on the substrate(Guan et al. 2014). This type of ink gives good quality printing across a range of non-porous substrates like plastics and metals, and can be used for printing of beverage can labels and credit cards. To achieve good printing performance, ink viscosity should be around 10 cP at operating temperature and the surface tension is required to be in the region of 23-29 mN.m-1 with a pigment particle size typically below 1 µm and pigment content by total weight not exceeding 10% (Yeates et al., 2011(Guan et al. 2014)).

Digital Textiles Inkjet Printing Inks, Color Fiber-Interaction and Finishing Techniques

There are basically four different types of dyestuffs that are now being commercially used for digital textiles inkjet inks with each category capable of printing a particular type (or types) of fiber. Table 3 gives a summary of the various colorants, their mode of interaction with fibers, coloristic properties and method of fixation.

Table 3: Digital Textiles Inkjet Printing Inks, Color Fiber-Interaction and Finishing Techniques

Colorant	Fiber Type	Color Fiber-Interaction	Coloristic Properties	Fixation	Reference
Pigment	All fibers	No interaction – complex surface polymer (binder) bonding mechanism	Good washing fastness Excellent light fastness, good rubbing fastness depending on binder content	Oven curing at 160-180^{0}C for 30-90 seconds	(King 2013, Schulz 2002)
Reactive dye	Cotton, silk and wool, linen	Covalent fiber bonding	Bright colors, excellent washing fastness, excellent rubbing fastness poor light fastness	Steaming for 90-120 ^{0}C for 8-30minute depending on steamer type, washing and drying	(Lewis 2011, Stempien et al. 2016, Yang and Naarani 2007, Soleimani-Gorgani, Najafi and Karami 2015)
Disperse dye	Polyester	Hydrophobic- solid state mechanism	Excellent light, washing and rubbing fastness, bright colors	Transfer press or "thermosoled" or oven cured depending on type of disperse ink	(Niaounakis 2015a, Noppakundilograt et al. 2010)
Acid dye	Nylon, silk, wool, leather	Electrostatic and hydrogen bonding with fiber	Bright colors, excellent light fastness, good washingand rubbing fastness	Steaming for 20-60minutes depending on steamer type at 20-120 ^{0}C depending on shade and fiber type, washing and drying (except leathers)	(Campbell 2008, Hawkins 2003),(Niaounakis 2015a)

Fixation plays a very important role in digital printing because once a fabric has been digitally printed; certain processing conditions process must be done to fix the ink permanently onto the fabric to ensure durability. The type of ink used in the printing process generally determines the kind of finishing treatment required to fix ink into/onto the substrate as shown in table 3. Digitally printed fabrics appear almost dry compared to the traditional screen printed fabrics due to the slow nature of the printing process. Meanwhile, there's the need for further drying in some instances to ensure proper fixation using various drying techniques(Cie 2015a). Supplementary heating systems are usually available when the fabrics are batched on a roll to expose them to the warm atmosphere in the room. In circumstances where the printed fabric is only required for photographs in a catalogue or sampling, it may not be necessary to fix the print(Cie 2015a, Daplyn S and L. 2003). However, in most cases, fixation and washing is necessary to ensure that printed fabrics posses the necessary quality parameters. This does not only ensure that the full fastness properties of the dyes are achieved, but also brightens the colors appreciably.

Rheology of Inkjet Inks

Rheology is the study of the flow and deformation of matter(Oyarzun 2000, Żołek-Tryznowska 2016b).Inkjet inks for textile printing should exhibit Newtonian behavior, determined by examining the shear stress and viscosity of the inks under various shear rates(Samane 2016). The ideal ink should exhibit constant viscosity as shear rate is increased while the relationship between shear stress and shear rate must be linear(Żołek-Tryznowska 2016b).The main parameters that govern the ejection process of inkjet printing are the surface tension, the viscosity, and the rheological properties of the ink. The rheology of ink is an extremely important parameter because it aids droplet formation through the nozzle in a controlled manner for any given inkjet technology (Żołek-Tryznowska 2016b, Dharmesh 2005)

Jetting Behavior and Droplet Formation

Ink design is often influenced by a range of factors such as jetting performance, operation reliability and stability in use and storage. Due to these factors inks are usually prepared according to various parameters determined by the head design (Tyler 2005). According to Blank et al.,(Blank 2004) the general requirements for inks, can be summarized as follows: Purity (to avoid blockage), particle size, viscosity; surface tension, conductivity (Continuous flow application), stability, pH Value, foaming/defoaming properties. They continued by listing the substrate and end user requirements as substrate orientation, fastness properties, wash stability, handle and compatibility with conventional textile printing. These assertions have been collaborated by number researchers in recent years (Cahill 2006, Jackson and Douglasbauer 2005, Cie 2015b, Pekarovicova 2016b)

The tail or ligament that comes up with the ink drops during droplet formation is required to be absorbed by the head during its fall, otherwise several drops may formed and land in different places on the substrate which may impair print quality. There is still a possibility of spatter as the drop jets on to the substrate even if heads and tail merge; so ink developers are required to keep a balance between controlled dot gains and overspreading. Viscosity, surface tension and drop size are key variables to maintain this balance. Moreover, the pressure and molecular weight of the gas through which the drop falls play a vital role in addition to the viscosity(Xu 2005, Mills 1994). Table 4 gives the indicative requirement for accurate jetting for various inkjet-printing machines.

Table 4: Indicative Inkjet Ink Requirements (Xu 2005)

Ink Properties	CIJ Binary	CIJ Multi-Deflection	DOD Piezo	Valve-Jet	Office Piezo	Office TIJ
Viscosity (cP)	1.5	1-10	5-30	100	1.5	1-3
Surface tension (dyne/cm)	>35	25-40	>32	>24	>35	>35
Maximum particle size (Microns)	1	3	1	5	1	0.2
Conductivity (Micro Siemens)	Yes >500	Yes >100	No	No	No	No

Beyond these indicative requirements, Xi 2008 investigated the effect of signal amplitude and jetting frequency on Newtonian inkjet ink using CCD sensor and found that signal amplitude significantly affects the length of the ejected liquid thread, but does not affect the shape of the leading part and the higher the signal amplitude, the longer the liquid thread formation and the larger the ejected liquid volume as can be seen from figure 2.

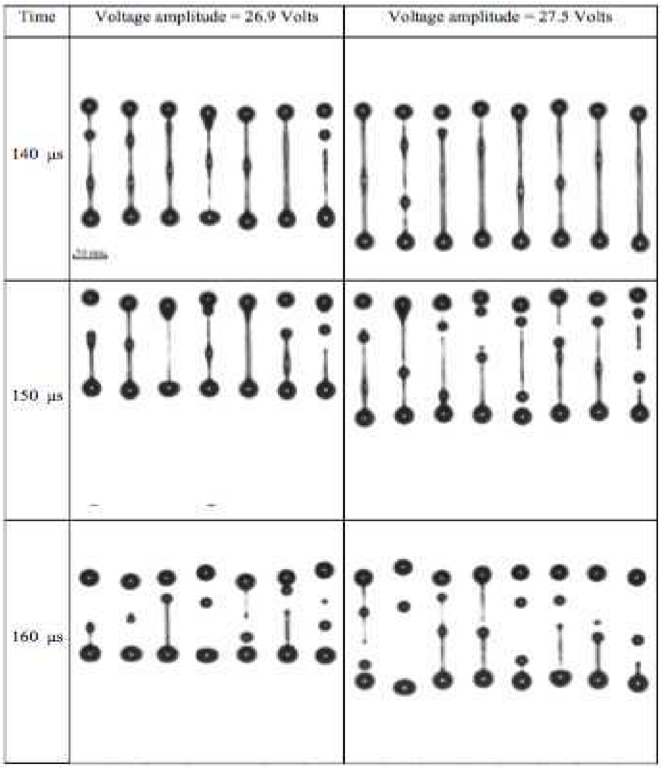


Figure 2: Effect of Voltage Amplitude on Secondary Thread Formation (V = 26.9 and 27.5 Volts and Time Intervals of 140, 150, and 160 µs).Adapted from (Xi 2008)

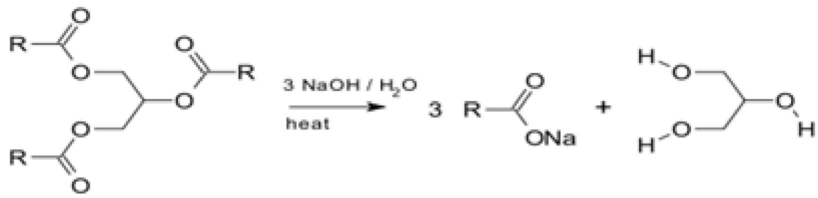
Similarly, (Dong 2006)asserted that satellite formation from Newtonian inkjet inks during DOD ejection remain basically the same due to end-pinching at the lower voltage amplitudes, but as voltage amplitude increases, the ligament length also increase leading to a multiple breakup as a result of the wave-like instability. Both researchers (Dong 2006, Xi 2008)concluded that jetting frequency have a significant effect on DOD drop formation dynamics because as jetting frequency remain low, DOD drop formation remain the same but at sufficiently high jetting frequency, the propagating wave induced by consecutive pulses interact with each other in the inkjet nozzle before being damped out, leading to a frequency dependent jetting behavior which substantially affect the volume and speed of ejected liquid body.

IMPORTANT PROPERTIES OF INKJET INKS

Viscosity

Schulz asserts that viscosities must be adjusted in such a way to produce a flow that is high enough to avoid starvation at the nozzle as well as not so high that it flows out on the nozzle plate. (Magdassi 2010) postulated that viscosity greatly affect the size of the droplet and drop speed. If drop speed is too low, then there is a possibility of drop deflection on its way to drop formation on the substrate by air currents; thus affecting the print quality. Viscosity modifiers play a very important role in increasing the reliability and quality by controlling the drop formation and break-up process. If the molecular weights of viscosity modifiers are very high, then jet break-up become difficult because of their elasticity(Syed 2016). There are several viscosity modifiers available, of which glycerol, Polyethylene Glycol of molecular weight 200 (PEG200) and Carboxymethyl Cellulose (CMC) are some examples. Polyethylene glycol (PEG) is a synthetic polyether, which is available in a range of molecular weights. Low molecular weight PEG is a clear, viscous liquid product with molecular weight lower than 10,000, whereas polyether with molecular weight higher than 10,000 is known as polyethylene oxide (PEO) (Bin Bao 2016). Similarly, CMC is used as a viscosity modifier or thickener, and to stabilize emulsions in various products including textiles printing inkjet inks(Heinze 2005, Lic 2002). It is also a constituent of many non-food products, such as toothpaste, laxatives, diet pills, water-based paints, detergents, textile sizing, and various paper products(Jackson and Douglasbauer 2005, Magdassi 2010). It is used primarily because it has high viscosity, is non-toxicity.

Glycerol, which has molecular formula of HOCH2CHOHCH2OH, is also colorless viscous solution belonging to the alcohol family of organic compounds (Rosen 2004). Natural or native glycerol can be obtained as a by-product in the conversion of fats and oils to soaps as shown the scheme 4 below whereas synthetic glycerol can be produced from propylene. The fastest growing method of producing glycerol is from the conversion of fatty acid methyl esters for biodiesel, where 100 kg of glycerol is formed in 1000 kg of biodiesel (Spinelli 1998).



Scheme 1: Production of Glycerol as a Co-Product in the Production of long-Chain Carboxylate Salts

These viscosity modifiers help inkjet textiles printing ink maintain stable viscosity which ensure constant jetting pressure and ensure less nozzle clogging (Niaounakis 2015a). The quantity of viscosity modifiers used in a particular formulation is dependent on the type of colorant being used, the kind of inkjet machine and nozzle i.e DOD or CIJ and the target textiles material to be printed (Ujiie 2006).

Surface Tension

Surface tension is one of the most important properties of ink jet inks for textile applications. Its been suggested that surface tension of ink is a primary factor determining droplet formation and spreading on the substrate upon contact(Magdassi 2010). Ideally, ink jet inks should have a surface tension in the range of 25-60 dynes/cm(Ujiie 2006, Cie 2015b). Surface tension can be controlled by using surfactants and by selecting proper solvent compositions. For example, adding propanol to water will cause a large decrease in surface tension, from 72.8 dyne/cm to below 30 dyne/cm, depending on the propanol concentration. Surface tension of the inks must be in the range (25-60 dynes/cm) so it wets the capillary channels, flows through the nozzle and forms the droplets correctly to ensure proper jetting(Le 1998, Ali 2008).Surfactant also called surface-active agent are substance such as a detergent that, when added to aliquid, reduces its surface tension, thereby increasing its spreading and wetting properties. In the dyeing of textiles, surfactants help the dye penetrate the fabric evenly(Mallinson 1999). They are used to disperse aqueous suspensions of insoluble dyes and perfumes. The surfactant possesses two different chemical groups, one compatible with the liquid to be modified, and the other having a lower surface tension. Typically, 1% or less issufficient enough to efficiently lower the surface tension of inks, coatings, and paints(Mallinson 1999).

Fluor chemicals, silicones, and hydrocarbons are common categories of surfactants, which are capable of lowering surface tension of any material and are the most efficient wetting agents. Silicones are next in efficacy and are lower in cost but certain types of silicone, however, can become airborne, causing serious environmental problems and as well contaminate the substrate (Flick 1993, Toshio 1963).

Although it may be required to lower the surface tension of a coating, the opposite is true for the substrate because the very agent that helps the decorating material renders the substrate useless. Silicone contamination produces the infamousdewetting defect called “fish-eyes.”Coatings, paints, and inks, once modified with surfactants, are usually permanently changed, even after curing(Flick 1993). Their low surface energy will make them difficult to wet over if, for example, it is necessary to apply a top coat. There are several options for overcoming this problem. The best practice is to use the smallest amount of the least potent surfactant that will do the job by starting with the hydrocarbon class(Mallinson 1999, Magdassi 2010).

It’s also been suggested that the substrate on which the silicon induced ink is going to be applied should be clean (Toshio 1963). Another possibility is to use reactive surfactants possessing a functional group that can react with coating making the binder less active after curing (Toshio 1963, Mallinson 1999). Once the surfactant has completed the role of wetting agent, it is no longer needed. One other approach is to add surfactant to the second material to be applied(Flick 1993).

Humectants

Humectants are mainly used to control or limit the evaporation of the inks(Pekarovicova 2016a). Humectants such as glycols and alcohols act as hygroscopic agents to remove moisture from the air during printing or in the idle position of printer, thus preventing clogging of print heads (Jackson and Douglasbauer 2005, Cie 2015b).

Foaming and Defoamers

A severe problem in ink performance is the presence of bubbles in the ink (Magdassi 2010, Karl Fink 2013).Foaming is often observed in inks, which contain surfactants and polymers. A common solution to this problem is addition of a defoamer, which is a molecule that causes breakdown of foam, which is already present. The defoamers act by reducing surface tension in a local area to very low values, causing these local areas to be thinned rapidly (example: amyl alcohol); and by promoting drainage of liquid from the lamellae (example: tributyl-phosphate which reduces surface viscosity)(Kelvin 1977).

Should the need arise to severe foaming of ink, it is necessary to seek defoamers which do not separate out during prolonged storage, and use concentrations as low as possible (Karl Fink 2013). Antifoaming agents are often based on mineral oils (hydrocarbons). Typical active ingredients of alternative products are silicones, phosphoric acid esters (especially. tributylphosphates), fatty acid compounds, high molecular alcohols, fluorine derivatives, and mixtures of these components*(Wassim Kaimouz 2010).*

Dielectric Properties and Conductivity

Ink conductivity is also important for printing systems in which ink recirculation sensors are triggered by conductivity signals obtained by contact of the sensor with the ink (Blank 2004, Pekarovicova 2016a). These properties are essential for continuous inkjet inks, in which the droplets are deflected due to an electrical field. The charging ability is obtained by adding charge control agents like electrolytes and ionic surfactants, which are soluble in the ink medium. The conductivity should be very precisely controlled such that any slight variation in conductivity during storage should be prevented. Variation in conductivity may occur due to salt precipitation, interactions with other c components and the wall of the container(Bin Bao 2016, Gregory 1991).

pH and Electrolytes

The pH is important in water-based inks and may significantly affect the solubility of the various components and the stability of the dispersed pigments. The solubility effect is often observed when the ink contains a polymeric binder such as acrylic resin, which is insoluble at low pH(Campbell 2008). Colloidal stability is affected by the zeta potential of the particles: the higher the value the higher the stability (Magdassi 2010, Ali 2008). He further stated that adsorbed polymers, which are effective while they are charged, achieve stabilization; the charge is usually dependent on the pH of the system. Therefore, some ink formulations contain buffers, which make the ink less vulnerable with regard to slight variations in ink components and water quality(Pekarovicova 2016b).

The presence of electrolytes can cause severe stability problems during prolonged storage, due to compression of the electrical double layers of the particles (which may cause flocculation); therefore the concentration of electrolytes must be very low (Cie 2015b). This is especially important for multivalent electrolytes, such as calcium. Consequently, it is essential to control the water quality and sequestering agents such as EDTA(Dominioni 2003).

Ink Storage and Stability

All properties of textiles inkjet printing inks including pH, viscosity, surface tension, particle size and its distribution in the case of dispersed colorant, and dielectric properties should remain constant over a prolonged period of time ("shelf life"), which is typically two years at room temperature, but exceptions certain inks like UV inks. Once the ink is prepared, it should meet specific physicochemical criteria, which depends on its intended use (Magdassi 2010, Ali 2008). The main parameters considered while preparing the ink discussed above should remain constant over the shelf life of the ink. A stable ink is an ink in which all its properties remain constant over time (Lin 2004, Ujiie 2006). In most cases, inks which do not contain un dissolved materials, instability is caused by interactions between the ink components, such as polymerization in UV ink, precipitation and phase separation due to changes in solubility (encountered, for instance, when samples are stored or shipped at low temperatures), and even interaction with the walls of the ink containers(Guan et al. 2014, Li 1999). Another cause of instability could be the adsorption of wetting agent from the ink onto the polymeric walls of the container, which may result in an increase in surface tension, or partial polymerization of monomers during storage. Such happening could lead to an increase in ink viscosity. For inks, which contain pigments, the most common problem is aggregation of the pigment particles due to the inherent instability of most dispersion systems (Ujiie 2006). Pigment dispersions stabilization mechanisms has been extensively discussed by Oyarzun 2000.

Fabric Pre-Treatment Methodologies for Digital Textiles Inkjet Printing

Fabric pre-treatment is indispensable to the achievement of good color strength, excellent fastness, droplet control, color penetration and spread for optimum image quality in digital textile printing especially with reactive dyes (Wassim Kaimouz 2010, BSF 2003, Zhu 2011). This process is necessary because ink-jet printing of textiles has generally been carried out using pretreated materials with the exception of carpets. It is common knowledge that traditional auxiliaries required such as urea, alkali and migration inhibitors cannot be incorporated into the inks(Pal 2011, Cie 2015c). More so, commercial digital textiles inkjet reactive inks are usually based on dyes with low to moderate fixation properties (generally mono functional reactive dyes), so it is imperative to boost dye fixation for technical, economic and environmental reasons. As a result, most substrates are pre-treated with different agents with different mass fractions to enhance maximum absorption before ink-jet printing. The pretreatment chemicals range from natural to synthesized chemicals. Fabric pretreatment plays a very important role in how the inks interact with the substrate and the consequent coloristic properties. Table 5 gives a summary of the various pretreatment technologies applied on various fabrics with their associated colorant inks.

Table 5: Pretreatment for Digital Textile Printing

No.	Pretreatment Chemical Used	Type of Colorant	Substrate/Fabric	References
1.	Alginate ester/seaweed	Reactive dye ink	Cotton	(Zhu 2011)
2.	Urea/alkali/lyoprint R.G	Reactive dye ink	Cotton/lyocell	(Wassim Kaimouz 2010)
3.	Atmospheric pressure plasma (APP)	Reactive dye ink	Cotton	(Chunming and Kuanjun 2009)
4.	Plasma treatment using Radio Frequency O_2Frequency Plasma (RFOP)	Pigment ink	Polyester	(Chunming 2015, Wang et al. 2009, Chunying 2010)(Fang and Zhang 2009)
5.	Enzymatic treatment	Disperse dye ink	Polyester	(Ibrahim 2012)(El-Hennawi et al. 2015)
6.	Chitosan	Reactive dye ink	Cotton	(Choi 2005)
7.	Gas plasma	Pigment ink	Cotton	(Pransilp et al. 2016)
8.	Foam	Pigment ink	Silk	(Shen et al. 2014)
9.	β-cyclodextrin and citric acid	Pigment ink	Polyester	(Chen et al. 2012)
10.	Fluoroacrylate copolymer and Guar Gum	Disperse dye ink	Polyester	(Chang and Chao 2009)
11.	Nano-modification using atmospheric-pressure air/Ar plasma (AAP)	Pigment ink	Polyester	(Chunming 2015)
13.	Amino compounds	Pigment ink	Silk	(Phattanarudee, Chakvattanatham and Kiatkamjornwong 2009)
14.	Ebecryl 2002 polyurethane acrylate (PUA) based on PEG	Pigment ink	Viscose, nylon, wool, cotton, polyester	(El-Molla 2007, Niaounakis 2015b)
15.	Cationization with 2,3-epoxypropyltrimethylammonium chloride (EPTAC)	Reactive dye ink	Cotton	(Teng, Ma and Zhang 2010, Schindler 2004)
16.	Cationization with dodecyl trimethylammonium bromide (DTAB), tetra methyl ammonium hydroxide (TMAH)	Reactive dye ink	Linen	(Rekaby, Abd-El Thalouth and Abd El-Salam Sh 2013, Schulz 2002, Schindler 2004)
17.	Cationization with 3-chloro-2 hydroxypropyltrimethylammonium chloride	Reactive dye ink	Cotton	(Wang et al. 2009, Blank 2004)
18.	Tertiary amine cationic polyacrylamide	Reactive dye ink	Cotton	(Teng et al. 2010)
19.	Amino-terminated hyper branched polymer ($HBP-NH_2$)	Reactive dye ink	Cotton	(Fang and Zhang 2009, Zhang et al. 2008)
20.	Cationization with (3-chloro-2-hydroxylpropyl) trimethyl-ammoniumchloride (CHPTAC)	Reactive dye ink	Cotton	(Acharya et al. 2014)
21.	Pretreatment with polyamidoamine (PAMAM) dendrimer	Reactive dye ink	Cotton	(Niaounakis 2015b)(Cie 2015c)

Table 5: Contd,				
22.	BSF LupreJet HD	Disperse dye ink	Polyester	(BSF 2003)

Pretreatment is carried out to ensure maximum absorption and retention of dye, or ink, in just the right places to avoid "bleeding" and fading after washing.

Drying Mechanism of Inkjet Inks

Textile inkjet inks upon jetting onto substrates dries up through various mechanism depending on the ink type. The various drying mechanisms are absorption, evaporation or penetration (Le 1998)

Table 6: Drying Mechanism for Different Inkjet Inks (Le 1998)

Ink Type	Print Head Technology	Drying Mechanism
Aqueous	Thermal/piezoelectric	Continuous absorption Penetration absorption
Oil	Piezoelectric / continuous	Absorption/ penetration
Solvent	Continuous / piezoelectric	Evaporation
Hot melt	Piezoelectric	Solidification
UV curable-based	Piezoelectric / continuous	Polymerization
Reactive-based	Piezoelectric / continuous	Oxidation polymerization

Similar to the observation made by (Le 1998), other researchers have postulated that inkjet ink drying mechanisms are also influenced by the print head technology, the type of substrate, the pretreatment method and the kind of viscosity modifier employed in the ink formulation(Cie 2015b, BSF 2003).

Future Perspective

Advancement in inkjet technology has revolutionized the textile printing industry because it has notably eliminated the time and labor involved in plate-making and ink blending in conventional screen textile printing. This revolution will only be complete with good quality environmentally friendly inks that print all substrate and can offer superior coloristic properties. The potential for digital fabric printing grown exponentially over that last decade with researchers still finding new ways to further sped this growth with its low cost, fast turnaround, and unlimited flexibility, digital printing will take over the sampling and mass customization printing market. With advancements in software, hardware, and chemical technology being made coupled with active research by textiles chemist to develop universal set of dyes/inks suitable for digital inkjet printing on chemically diverse textile materials, it is obvious that digital printing of textiles will yield its full potential and assume the center stage in the textile printing. A universal dye/ink set will certainly decrease the complex inventory of colorants in the industry, reduce machine down time and minimize dye content in printing effluents.

CONCLUSIONS

"We are creating a universal set of dyes and chemicals that will enable inkjet printing on chemically diverse textile materials" (Ujiie 2005)

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