

A Background of Sublimation Transfer Versus Direct Disperse-Dye Inkjet Printing

When printers want to decorate synthetic materials, such as polyester, some polyamides (e.g. Nylon 6.6), and cellulose acetate, they typically print sublimation ink onto transfer paper and then transfer their reversed images with heat and pressure. They might also print directly with disperse dye, fix the dye to the material with heat and perhaps wash, or they print with pigmented ink and cure the printed image. Each of these methods offers both advantages and disadvantages for possible applications when compared with the other methods. The following article describes sublimation and disperse dye inkjet printing, how they came to be, their strengths, limitations and applications.

Sublimation dye is chemically disperse dye, and inkjet disperse-dye inks are also often used to print sublimation transfers. Disperse dye is organic colorant material that lacks ionizing groups and has low water solubility. These characteristics enable them to dye and fix to hydrophobic materials and are currently the only low water-soluble dyes that dye polyester and cellulose acetate. Also, disperse dyes have some of the smallest molecules of dye types with structures that are planar and non-ionic.

Synthetic polymeric chains of polyester form tightly packed crystalline structures that are not receptive to the large molecules of the ionic dyes that are used to color and decorate natural fibers and fabrics, such as cotton, linen, wool and silk. But the shape and size of disperse dyes enables them to disperse their molecules between polyester's tightly packed polymer chains. Additionally, with heat and pressure, the synthetic polymer structure of polyester and other synthetic materials open up to

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By Vince Cahill, President, VCE Solutions



accept the volatile disperse dye molecules, which the synthetic polymers encapsulate as they cool.

Disperse dyes vary and are often categorized according to low, medium or high energy based on the amount of energy needed to fix them to receptive substrates. Low-energy disperse dyes use small molecules with low molecular weight. Medium- and high-energy disperse dyes have comparatively heavier molecular weights. Sublimation dyes typically use low- to medium-energy dyes, while disperse dyes for dyeing and direct printing typically use medium- to high-energy dye. Inkjet disperse-dye inks that are sold for use both as sublimation transfer and direct disperse dye printing are commonly of the medium-energy variety. While low-energy disperse dyes can transfer and fix to substrates at lower temperatures than the higher-energy disperse dyes, their prints are more fugitive when exposed to sunlight.

Inkjet sublimation dye printing is different from inkjet direct-dye printing in a number of ways. Sublimation dyes print indirectly in reverse on transfer sheets and are then processed with heat and pressure to transfer the printed images and text to receptive substrates. Direct disperse-dye inkjet printing, on the other hand, eliminates the need for transfer paper or other carries materials, and prints images directly onto substrates.

The sublimation transfer process uses heat and pressure to sublime, i.e. change the dye from a solid to a gas without passing through the intermediate liquid phase. The dye in its light- to medium-weight molecular and gaseous form readily penetrates synthetic materials that the transfer heat and pressure process has opened to be more receptive. Lighter molecular weight dyes require less heat to sublime and are more suitable for transferring to heat-sensitive fabrics that the heat transfer process could damage.

On a recent visit and tour of Chem Cubed's operations at the State University of New York — Stony Brook's Advanced Energy Center, I asked Daniel Slep, PhD Chemist and Chem Cubed's Chief Technology Officer and Founder, about his past work at Hilord. During that period he spent time formulating disperse dye inks, and explored the advantages of indirect sublimation inkjet printing versus direct disperse-dye inkjet. Dr. Slep told me that he had experimented with and formulated many types of disperse-dye inks using a broad range of carriers, including organic solvents, oil, water and UV-curable chemistries. He indicated that both indirect inkjet sublimation and direct disperse-dye printing offered effective solutions for printing polyester and other synthetic materials. Sublimation worked best for small-sized projects such as decorating promotional products. Direct

disperse-dye printing offered advantages for large-area prints, including roll-to-roll fabrics and soft signage banners. He noted that sublimation transfers eliminated the need for post-print washing, while direct disperse-dye prints that would be worn should be washed to eliminate residual dye before a person wears them.

On one hand, sublimation inkjet printing requires the use and expense of transfer paper, heat transfer press and their operators, while on the other hand, direct disperse-dye inkjet printing may require pre-coating on the media. Sublimation transfers are less expensive to distribute to distant locations where they would be transferred. They also carry less risk than a large direct printed roll of fabric. But direct printing can save time and the labor involved in heat transferring images. Dr. Slep concluded that both methods could provide cost- and performance-effective solutions, depending on the nature of the applications and availability of the capital equipment and staff trained in the use of each process.

The development of synthetic fibers, which the available conventional dyes could not color, drove the efforts to develop dyes that could. While dyes have been around for millennia, discovering synthetic dyes that would fix to the new synthetic fibers required a few generations. Archeological evidence traces humans dyeing yarn and fabrics with plant matter for indigo, madder, woad and insects for Tyrian purple as far back as the Neolithic Period. In 1856, William Henry Perkin discovered the first human-made organic dye, which in turn lead to the creation of over 10,000 synthetic dyes today. Industrial production textile dyers replaced the natural dyes with the arriving synthetic ones for printing natural fiber fabrics due to their typically lower cost, greater color range, brightness, superior fastness and durability and ease of application. The early synthetic dyes for coloring natural fibers were ionic in nature and could attach themselves and be fixed in a non-covalent manner to oppositely charged portions of the natural fiber molecules. Cellulosic fibers, such as cotton and linen have hydroxyl -OH reaction sites while protein fibers, such as wool and silk offer -NH3 Lewis structure sites, where oppositely charged portions of dye molecules can attach. Dr. Ray Works in his December 2009 article in Signs and Digital Graphics, entitled Sublimation for Beginners, described these reaction sites on natural fibers as "hooks" to which conventional dyes could fix. But conventional synthetic dyes that color natural fibers will not attach, however, to synthetic fibers like cellulose acetate and polyester because these synthetic materials lack the ionic "hooks" that natural dyes require. In 1954, Rattee and Stephens at Imperial Chemical industries (ICI) invented fiber reactive dyes that could covalently bond to cellulose and protein fiber reaction sites. Other natural and synthetic dyes fixed to fibers without covalent bonding, instead fixed with physical capture, hydrogen bonding, ionic bonding as with acid dyes or Van der Waals forces.

The development of disperse and sublimation dyes begins with the discover of the materials they would dye.

The Path to Inkjet Sublimation & Disperse-Dye Printing

The historic path from the first synthetic material and fibers, however, took decades to develop and commercialize. Paul Schützenberger, (1829–1897), a French physician and prolific chemist, reported formulating one of the first synthetic materials, cellulose acetate, in 1865 . In 1904, Camille Dreyfus (1878–1956) and his brother Henri (1882–1944) of Basel, Switzerland experimented with cellulose acetate and developed a cellulose acetate film for the early silent motion picture industry, as well as an acetate lacquer for coating the fabric skin of early aircraft. In 1913, they produced the first continuous filament yarn of cellulose acetate, which they named Celanese. Unfortunately World War I erupted during that year, delaying the commercial development of cellulose acetate fibers and the formulation of dyes that could color them.

In 1922, British chemists, Green and Saunders developed an azo-based dye that could color cellulose acetate fibers, but had short comings for consistent dye production. In 1924, Baddiley and Ellis formulated sulpho-ricinoleic-acid (SRA), with which they dyed cellulose acetate fibers. SRA was employed as dispersing agent, which decades later resulting in the name, disperse dye. Subsequently, SRA was discovered to be able to dye polyester, polyamide (Nylon), acrylic and other synthetic materials.

Dr. Justin Hayward, Founder Director of Cambridge Investment Research Ltd., recently traced an early form of sublimation transfer printing back to the 1929 to 1930 period when Kartaschoff at British Celanese Ltd. observed the coloring of cellulose acetate when placed in contact with disperse type dye under heat. Reportedly, Wallace H. Carothers (1896–

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1937) of DuPont had found that alcohols and carboxyl acids could be mixed to make early polyester fibers, but his discovery of polyamide pushed his polyester work from his laboratory's priority list and his death at age 41 left much of his work for others to complete. Meanwhile in 1941, 12 years after Kartaschoff's discovery of a dye that could sublimate into cellulose acetate, British scientists John R. Whinfield, James T. Dickson and their employer, the Calico Printer's Association of Manchester, UK, patented polyethylene terephthalate — now abbreviated as both PET and PETE, the most used polyester resin and primary recipient of sublimation and disperse dye coloring. Britain's Imperial Chemical Industries (ICI) first manufactured polyester fibers. In 1946, DuPont purchased rights to polyester fiber. By 1951, ICI offered polyester fiber under its Terylene trademarked brand and DuPont offered it under its trademarked Dacron brand. These relatively inexpensive fibers offered desirable characteristics, which led to markets adopting them.

The development of polyester fibers, fabrics and films soon led to the commercial development of dye-sublimation printing. Hayward notes that around 1950, the Italian company Star Stampa Artistici di Milano "used a multi-coated paper substrate as a transfer medium in a melt process at high pressure, using gravure." By 1957, "Noël de Plasse, of the Lainière de Roubaix company in France, working with Filatures Prouvost Masurel, invented dye-sublimation printing." They founded Sublistatis SA to promote their invention. Also, DePlasse observed that the disperse dyes sublimed, i.e. changed from a solid to a gas without passing through the liquid phase.

Conventional analog gravure and lithographic offset printing of dye sublimation dye sublimation transfers to decorate synthetic soft and hard surfaces grew during the 1960s and '70s. The Photographic industry also developed sublistatic dye-coated ribbon-based print systems for printing photos directly.

Hayward estimates that, "By 1970, 24 million square meters (m^2) of transfer papers had been produced." He also reports that by "the mid '70s, production of transfer papers had risen rapidly to around 350 million meters, and a third of printed polyester was analogue printed by the transfer method." Computer controlled print methods also began to print sublimation transfers including impact monochrome dot matrix devices, e-stat presses, laser electro-photographic printers, thermal transfer, continuous and drop-on-demand inkjet. The mid-1970s the work of Wes Hoekstra at the Jet Propulsion Laboratory at Pasadena, California ushered in the arrival of computer controlled electrostatic printing of sublimation toner for imaging transfers in the early 1980s.

Milliken's 1975 introduction of its Millitron computer controlled roll-to-roll carpet printer and Zimmer's 1976 debut of its roll-to-roll ChromoJet spot color carpet printer used valve-jet type for application of disperse dye onto synthetic carpet fibers, primarily polyester and also cationic dyes for cationic dye receptive polyester and acrylic. Zimmer subsequently built its process color Chromojet and adopted inkjet systems for its Colaris line of carpet and fabric printers.

Promotional and novelty products and custom print providers adopted various digital sublimation methods to customize messages on their products. In 1983, Roy Devries, currently of ScreenTrans in Moonachie, New Jersey, partnered to form RPL Supplies to provide sublimation technology and supplies to the advertising specialties and print markets. In 1985, he established ScreenTrans where he, his chemist Henry Lewis, his family and staff refined both screen and inkjet printing of sublimation dyes to print and convert polyester fabric to make banners, flexible signage and displays for indoor and outdoor advertising, point of sale, and exhibition applications. ScreenTrans developed darker sublimation blacks and more vibrant colors than were generally available. Their in-house ink formulation capability provided them with the ability to adjust sublimation inks to match color requirements of their New York City area corporate, advertising and design communities.

Nathan Hale formed Sawgrass Technologies* in 1988 as a software and systems integration business in Columbia, South Carolina. The company moved to the Mt. Pleasant-Charleston, South Carolina area in 1990 where it refocused its efforts on sublimation ink and systems for digital decoration. Venture capital executive, Steven Carnevale and chemist, Ming Xu, PhD, added their resources and expertise in positioning the company for its major patent role cornering the digital inkjet sublimation market.

In 1989, Seiren of Fukui, Japan established its Viscotecs division that built an inkjet printing facility and business for printing short-run and custom orders. Seiren developed custom marketing under its Viscotecs label. In addition to inkjet

printing natural fiber fabrics, Viscotecs inkjet direct printed manmade fabrics with disperse dyes. The company focused on printing custom vehicle interiors, short-run active and swimwear, fashion apparel, and signs and displays. Much of the Viscotecs production centers on polyester and other synthetic fibers and disperse dyes.

Development of inkjet technology for textile printing continued to expand application possibilities for all textile dye-based types and pigmented inks. Reactive dyes in Jos Notermans, the Commercial Manager for Digital Textiles at Stork's SPGPrints*, noted that Stork had formed by the end of 1986 a project team to study digital technologies for printing textiles, confirming that inkjet was the most probable to replace rotary. In 1991 at the International Textile Machinery Association (ITMA) exhibition in Hanover, Germany, Stork introduced its Trucolor TPC high resolution continuous inkjet (CIJ) proofing printers based on Professor Hertz of Sweden's Lund University CIJ design principles with a Stork patented nozzle system. The Trucolor TPC printed a sample sized piece of fabric or sheet of paper that was taped to a drum that rotated under printheads traversing along a horizontal axis. The original printed 1 m^2 of printed material per hour (h).

At the 1995 ITMA exhibition in Milan, Stork exhibited the only textile inkjet printer, a similar CIJ printer that at a rate of 6 m^2/hr. At the 1999 ITMA in Paris, where seven inkjet textile printer manufacturers exhibited, Stork unveiled its Amethyst roll-to-roll CIJ textile printer that produced 20 m^2/hr. At the following 2003 ITMA at Birmingham UK, 23 inkjet textile printer manufacturers exhibited. By the late 1990s, Mimaki's* first textile printer with Epson PIJ printheads won Italian silk print industry adoption for short-run print production of high end silks. A number of Italian textile equipment companies fitted the Mimaki print engine on their sticky belt fabric carrier systems.

DuPont* introduced its Artistri prototype PIJ roll-to-roll textile PIJ printer in 2001. A number of attempts at textile inkjet systems failed to gain market acceptance. Canon* had built only two of its WonderPrint "bubble jet" thermal inkjet (TIJ) textile roll-to-roll textile 6-color hexachrome printers. Encad's TIJ textile printer business never gained market traction and faced competition from the higher resolution Mimaki textile printers. Many of these early inkjet systems offered their users a choice of reactive, acid and disperse dye inks. During the first decade of the 21st Century, the eight printhead DuPont Artistri roll-to-roll textile inkjet printer, Reggiani DReAM, Robustelli Monna Lisa, Konica Minolta Nassenger, MS*, Durst* and other inkjet printer manufacturers opened the door for direct inkjet textile printing, including disperse-dye inkjet printing of polyester fabrics. Major inkjet equipment manufacturer EFI Vutek partnered with ink formulator Hilord to offer a solvent-based disperse dye ink for printing sublimation transfers on EFI* Vutek's TX3250r. They introduced a prototype version of the printer at the SGIA Expo in 2010 and commercialized it in 2011.

Korean company d.gen evolved from a software and Roland reseller to develop and manufacture its own digital textile printing systems. In 2003, it established its European branch near Milan, Italy and tapped into Italian expertise and experience building inkjet textile printers. In 2004, it introduced its Teleios direct print and fixation inkjet printer. It expanded its Teleios line of direct disperse-dye inkjet printers with the launch of its Teleios Grande 3.3-meter system at ITMA in 2011. In 2012 at the Fespa Exposition in London, it launched its Papyrus dye-sublimation transfer printer. Kilhun Lee, d.gen's CEO, and Andrea Negretti, d.gen's Vice President and Worldwide Business Manager, focused much of the company's development toward direct disperse dye and sublimation transfer inkjet printing. They have advanced direct printing of disperse dye for soft signage on polyester, while in addition offering reactive and acid dye sets and pigmented inks for home furnishing print applications.

At ITMA in Milan during November 2015, single-pass inkjet textile printing captured the attention of the attendees and headlined press accounts. In addition to printing acid and reactive dyes, manufacturers of single-pass printer were also offering or developing disperse dyes for use in their production equipment. Mimaki, d.gen, Epson*, Roland*, Mutoh*, EFI, MS, Konica Minolta and others are bringing dye sublimation and direct disperse-dye printing solutions to market. Throughout exhibitions halls, retail stores and on lamp posts in towns and cities around the world inkjet printed polyester soft signs and banners proclaim the importance of inkjet indirect and direct disperse-dye decoration. Inkjet



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provides the flexibility and cost and time advantages over analog print methods. While the analog textile printing market has matured, inkjet textile printing continues to grow providing colorful solutions that meet current and prospective market demands.

[1]Barber, E. J. W. (1991). Prehistoric Textiles. Princeton University Press
[2]https://sdgmag.com/features/sublimation-beginners
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[4]http://textilelearner.blogspot.com/2012/01/disperse-dye-history-of-disperse-dye.html
[5]https://www.linkedin.com/pulse/brief-history-dye-sublimation-printing-dr-justin-hayward-hayward
[6]Ibid
[7]Ibid
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[9]Ibid
[10]Jos Notermans, 25 Years of Digital Printing, Fabric Graphics, January 2012
[11]David J. Tyler (2005): Textile Digital Printing Technologies, Textile Progress, 37:4, 1-65

***SGIA Member Companies, in order of mention:**
Sawgrass Technologies, since 1998
SPGPrints, since 2012
Mimaki, since 1999
DuPont, since 2006
Canon, since since 2006
MS, since 2013
Durst Image Technology US LLC, since 2002
EFI, since 1998
Epson, since 2006
Roland DGA, since 1995
Mutoh America Inc, since 1991

Vince Cahill is President of VCE Solutions, which provides consulting services for Fortune 500 and other companies operating in the analog and digital printing industries. He has also served as a Principal of The Colorworks, where he had a 25-plus year career in specialty graphics. Cahill also served as CEO of Datametrics Corp. as well as Principal and Technology Developer for Newhill Technologies and Specialty Materials. He is a longtime volunteer with SGIA, serving on the Association's Textile Committee for several years. Cahill has contributed several articles to the SGIA Journal. He is also a member of the Academy for Screen and Digital Printing Technologies.

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