Surface science in photography

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Advanced surface science and material technologies are the basis of industrially manufactured photographic print media from its beginning in the early 20th century up to now. This paper traces the history of nanotechnology in photography and particularly at ILFORD. ILFORD is one of the pioneers of industrial black and white photo manufacturing, with more than 130 years of history. ILFORD Imaging Switzerland, the Swiss branch of ILFORD, manufactured high quality colour photo display film for over 40 years (1972–2013), and photo inkjet media in industrial quantities from 1996–2013, at their site in Marly (Fribourg). A mainly empirical craft until the early 20th century, photography quickly changed into a scientific discipline embracing the most advanced surface analysis techniques, colloid science methods and liquid multilayer coating technologies of its time. Starting around 1990 those same skills were applied to large-scale manufacturing of photo-like inkjet media and ink, the "digital" photographic media that freed the photographer from the darkroom and presented unforeseen creative opportunities to the artist.

1. Introduction

Photography is generally not considered as a branch of nanotechnology. Starting as a craft and driven by enthusiastic and creative inventors in the late 19th century, photographic film and paper development had changed into an empirical industrial process by the turn of the century.[1] While it is possible to capture an image of a still object with long exposure times on a rather simple hand-made black and white film or paper, sophisticated surface treatment and nanostructures are needed to create the photosensitive silver halide grains that enable capturing the light from analogue high speed cameras, microscopes, telescopes and from the everyday consumer camera in black and white and colour. Those engineered silver halide grains also formed the basis of two new art forms that appeared in the 20th century, colour display prints and cinema colour films.[2] The scientific knowledge gained in photographic media development promoted progress in many other technical areas such as colour and imaging science and

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[1] B. Lavédrine, *Photographs of the Past*. Los Angeles: The Getty Conservation Institute, 2007.

[2] M.R. Peres (ed.), *Focal Encyclopaedia of Photography*, 4th edn. Burlington, Mass.: Focal Press, 2007.

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metrics[3,4] vision,[5] surface analytical instrumentation and particle sizing, colloid science[6] and high speed multilayer coating[7] as well as coating inspection.[8]

The impressive progress in colour negative silver halide knowledge was driven by a small group of companies, the chromogenic colour photo manufacturers (Kodak, Fuji, Polaroid, Konica, Mitsubishi, AGFA, Ferrania, 3M). It was very difficult for newcomers to enter into this field as it needed massive resources to compete. On the other hand, the worldwide colour paper and film business provided considerable funds for research and development. Very large sales volumes and large scale production were needed to keep the highly automated factories with their skilled workers and with their experienced support personnel economically viable. With the decline in silver halide photographic print consumption, the installations were often no longer used at sufficient capacity and most of them have ceased to exist. While it is conceivable to make black and white photographic paper artisanally, it is not possible to make colour silver halide paper other than in an industrialized process. It is foreseeable that silver halide chromogenic paper will disappear, as have already Polaroid instant photo paper and Cibachrome/Ilfochrome chromolytic display film. Directly reprinting photographic colour negatives or positives in a dark room will thus no longer be an option. The colour silver halide photographic process will be a historical documentation and art form limited to a window of about 100 years, with its peak between 1970 and 2000.[9]

For all but some artistic or educational applications, direct exposure from analogue film originals has long been replaced by scanning, digitizing and printing.[10,11] Most commercial photo printers have used digital processing since the 1990s. Printing of the digital image at that time was mainly done on silver halide papers. Since about 2005, printing on inkjet paper or by electrophotography has replaced the light exposure process in all but the most productive and automated photographic print laboratories. Inkjet or liquid toner prints today achieve the look and feel of a traditional photo and surpass it in longevity. Even professionals can hardly determine the print technology unless they look at the enlarged print pattern.

In the wide-format display print market, inkjet prints represent the vast majority of the products used, leaving only one particular niche to traditional photography, namely transparent and translucent displays in light boxes, mainly for the advertisement of luxury goods such as cosmetics and jewellery. Inkjet with UV radiation curing inks have enabled indoor architectural applications and even outdoor extra-large prints on film, glass, foam board and metal with a longevity of many years, which were never the domain of traditional photography.[12]

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3 G. Wyszecki and W.S. Stiles, *Colour Science*, 2nd edn. Wiley, 2000.

4 R.W.G. Hunt, *Measuring Colour*, 3rd edn. Kingston upon Thames: Fountain Press, 1998.

5 E.H. Land and J.J. McCann, Lightness and retinex theory. *J. Opt. Soc. Am.* **61** (1971) 1–11.

6 R.B. McKay, Technological applications of dispersions. *Surfactant Science Series*. New York: Marcel Dekker, 1994.

7 S.F. Kistler and P. Schweizer, *Liquid Film Coating*. Springer, 1997.

8 E. Gutoff and E. Cohen, *Coating and Drying Defects*. Wiley, 2006.

9 Reproduktion in der Fotokunst—Erhalt des Originals, Neureproduktion oder Interpretation. Symposium der DZ BANK Kunstsammlung, www.dzbank-kunstsammlung.de/de/sammlung/symposium, 2014.

10 R. Hofmann, Fotokunst: Erhalten oder Ersetzen. *Rundbrief Photographie* **22** (2015), No 2, p. 54.

11 R. Fageth, The picture to print value chain. *Proc. 2nd Intl Symposium on Technologies for Digital Photo Fulfilment*, p. 70. 28 February–1 March 2009, Las Vegas.

12 H. Wilhelm, B. Stahl, K. Armah and C.B. Wilhelm, Test Methods for the long-term permanence behaviour of photographs and fine art prints made with large format flatbed printers using UV-

When digital media began replacing the light-sensitive films and papers, the photographic industry was quick to apply its knowledge in colloid science and materials to the new digital technology. High-quality inkjet paper uses the same type of paper base stock originally developed for a very different purpose in silver halide photography. In the late 1970s, out of the need for faster wet processing, the commonly used baryta paper was replaced by so-called resin-coated (RC) papers [sometimes called PE (polyethylene) papers]. Those were high-quality papers, onto which a thin polyethylene layer (tens of micrometres) was extruded on both sides. In a final base-making step, polyethylene can be embossed with a structured drum press to a very glossy, semi-matt or pearl finish. The PE extruded paper was afterwards coated with the light-sensitive photographic silver halide and colour layers (see Figure 2, right side). In the photographic development process after exposure, the paper inside the impermeable PE layers did not take up processing chemicals or water. As only the swell volume of the photographic layers was absorbed, RC photo papers used less processing chemicals and allowed faster processing. In addition, RC papers were dimensionally more stable than fibre papers, very glossy and showed no cockle upon contact with water. They did not require the final heat press treatment of fibre papers to even out paper deformation and curl.

In inkjet printing, the paper is not immersed in water or chemicals. Many manufactures tried to replace the rather expensive RC paper as a support by other paper types. However, none of those papers provided the excellent gloss and the dimensional stability and the look and feel that photo customers were used to. Thus, high quality inkjet photo papers today use a base paper originally developed for photographic wet processing.[13] Instead of the light-sensitive layers of photography, inkjet papers have a thick liquid absorption layer (ink-receiving layer) coated onto the impermeable RC paper substrate (see Figure 2, right side). Instead of surface-treated silver halide grains, surface-treated mineral oxide nanoparticles form the basis of the glossy receiving layers that make up glossy inkjet papers today.[14] The steep rise in quality and permanence that was seen in inkjet print media development was only possible due to the extensive groundwork that had been laid in photographic science. The move to digital photographic output started in about 1985 and took only 20 years to completion, with a range of paper products, inks and colorants, paper surfaces and materials much wider than photography had ever been able to offer.

2. Surface science in silver halide photography

The very complete handbook of photographic science and technology edited by T.H. James and C.E.K. Mees and issued from 1942 to 1977[15] was the reference of its time. It treated photographic silver halide chemistry in detail. The dispersion of silver halide in gelatin is called an emulsion in photographic terminology. Research and development was colloid science and

curable pigment ink. *Digital Fabrication and Digital Printing*, pp. 84–85. Philadelphia: Society for Imaging Science & Technology, 2014.

13 A. Lavery, Photo media for inkjet printing. *International Conference on Digital Printing Technologies* (NIP 25), p. 216. Vancouver, 2000.

14 V. Ruffieux, P.-A. Brugger, U. Fürholz, M. Schär and J. Reber, Nanoporous ink-jet photo paper with high dynamic range. Society for Imaging Science & Technology. *Proc. Conf. on Digital Fabrication*, p. 543. Louisville, Kentucky, 2009.

15 T.H. James (ed.), *The Theory of the Photographic Process*, 4th edn. New York: Macmillan, 1977.

technology at an industrial scale. It comprised many key elements of today's nanotechnology, namely making controlled-size particle dispersions on a submicrometre level and treating the surfaces of such particles with monolayers to fine-tune their properties for sensitivity, tonal range and processing speed.

The size of typical silver halide particles is important for their sensitivity to light but also for maximum resolution. A trade-off had to be made between resolution and exposure time. A larger grain has a higher probability to absorb the multiple photons needed to make a cluster of silver atoms that leads to the latent image. In X-ray film the silver grains have to provide high coverage, hence their diameter is in the several micrometres range, whereas colour film grains are around 500 nm and graphic arts film grains around 250 nm in diameter. Daylight films and holographic plates are true nanoparticulate silver halide dispersions with a size distribution around 20–30 nm. Most silver halide grains are surface-treated to enhance overall sensitivity. In this so-called chemical ripening, the grain surface is recrystallized and doped with traces of gold, sulfur and silver. This doped surface is the key to the high light sensitivity required by all modern applications of photography.

The size distribution of grains in the emulsion is important for the tonal range of the film. A monosized distribution of silver halide grains produces a binary (black/white) response to light; broad grain size distributions lead to a large tonal range of greys. Monosized emulsions are used for graphic arts films that are intended for sharp black and white dot reproduction; broad size distributions are used in low contrast paper for continuous tone pictures in consumer and portrait photography.

The chemically ripened silver halide emulsions underwent additional surface treatment to acquire spectral sensitivity over the whole visible wavelength range. The natural sensitivity of the silver halides extends from the UV to 420 nm for AgCl, to 450 nm for AgBr and to 520 nm for AgI. In 1872, H.W. Vogel invented the sensitization of silver halide grains to the wavelength of green light and later to red light, based on dyes. These so-called sensitizing dyes absorb the visible light and transfer the energy to the silver halide grain.[16]

The first discoveries of surface modification and light absorption mechanisms started to be made over 130 years ago. This was well before powerful structural analytical techniques in the micro- and nanoscale such as electron microscopes and particle sizers and good chemical analytical tools were available. Conclusions were drawn from careful observation of macroscopic effects, which limited the theoretical understanding of the photographic process. New emulsions and film layers were developed empirically using trial and error. Modern analytical tools that became available in the early 1950s spawned a wealth of understanding of the chemistry and physics behind the photographic process and resulted in great progress in the performance of light-sensitive film and paper from 1960–1990.

3. Industrial production of silver halide emulsions, films and papers

Remarkably, in spite of its complexity, the manufacture of silver halide emulsions for photography was mastered on a vast industrial scale at very high speed and very good

[16] R.E. Jacobson, S.F. Ray and G.G. Attridge, *The Manual of Photography*. Burlington, Mass.: Focal Press, 1988.

reproducibility. Typical colour film and paper had more than 10 layers of gelatin silver halide emulsions with a total thickness of about 10–30 micrometres.[16] At its peak, the worldwide consumption of consumer photographic colour paper was around 900 million m^2 per year, which corresponds to more than 6000 tons of surface-treated silver halide emulsions consumed annually.

The high-volume industrial photographic manufacturing process is automated to such an extent that labour costs are generally inferior to energy and raw material cost. RC paper base, layer compounds and silver are the major factors of overall cost. Black and white paper contains appreciably more silver than colour paper, since in black and white paper and film silver is not only the light-absorbing element but also forms the image. In colour paper, silver is only the light absorbing element, the image is formed by dyes and the silver is recovered and recycled in the development process. The very sophisticated but automated colour paper manufacturing process, in which more than 10 layers are coated in total darkness, delivered colour prints at a lower cost than the black and white four-layer process run under red light, because of the difference in the costly silver content.

4. Nanosized dispersions of dyes in silver dye bleach ILFOCHROME media

ILFORD Imaging Switzerland's colour photo technology was very different from the mainstream chromogenic colour photography. In the chromogenic process, colourless precursors react to become image dyes in the presence of silver during photographic development.[17] In the chromolytic ILFORD silver dye bleach (SDB) process, the dyes were present in the layer before exposure and were bleached out in the presence of silver in the development/bleach bath.[18–20]

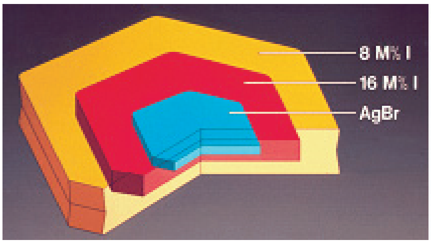
The SDB method as a direct positive process was used to make prints from slides instead of negatives. It made use of similar silver halide crystal growth techniques as the chromogenic process to make different types of grains. Multilayer grains, so-called core–shell grains, allowed adapting contrast, sensitivity and development kinetics. Figure 1 shows a schematic drawing of such grains and a scanning ion micrograph of an emulsion grain.

The SDB imaging dyes are very stable azo dyes of high purity. The archival (dark) stability of ILFOCHROME materials is rated as several hundred years,[21] which allows archival storage at normal temperatures, similar to black and white media and different from chromogenic materials, which should be kept in cold storage.[22] SDB images are very sharp as light scattered on silver halide grains in the layers during exposure is absorbed by the surrounding dye. On the other hand, the sensitivity to light is low. The speed of SDB film is not enough to be used as image capture camera film, but only as an enlargement medium.

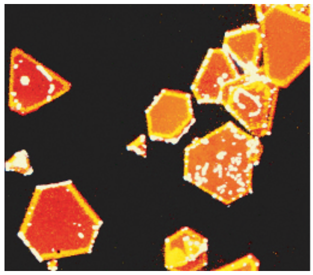
Photographic film coating is a liquid coating process in which many layers are applied simultaneously. It is important to suppress the diffusion of dyes into other layers of the multilayer

17 R. Shanebrook, *Making Kodak Film*. Rochester: 2010.
18 B. Coe, *Farbphotographie und ihre Verfahren- die ersten hundert Jahre in natürlichen Farben*. Bindlach: Gondrom, 1986.
19 A. Meyer, Silver dye-bleach color microfilm. *J. Appl. Photogr. Engng* **9** (1983) 117–120.
20 M. Schellenberg and H.-P. Schlunke, Die Silberfarbbleich Farbphotographie. *Chemie in unserer Zeit* **10** (1976) 131–138.
21 H. Wilhelm, *The Permanence and Care of Color Photographs*. Grinnell, Iowa: Preservation Publishing Company, 1993.
22 ISO 18920:2011—Imaging Materials—Processed photographic reflection prints—Storage practices.

The Long History of Surface Science in Colour Photographic Media:
Mastering Nanotechnology on an Industrial Scale.



A core–shell silver halide grain



Scanning ion micrograph of surface-treated silver halide grains. Orange=Br, yellow=I, white=Cl. The crystal near the lower right-hand corner is about 1 µm in diameter.

Figure 1. A core–shell (left) and surface-treated (right) silver halide grains.

liquid film assembly during manufacturing. In the late 1980s, ILFORD's research team invented azo dye dispersions by precipitating azo dye anions with alkaline earth cations. The dye aggregates formed needles with an aspect ratio of 1:10 and a width of less than 15 nm. It was most important to boost sensitivity for the red-sensitive layer on the bottom of the layer assembly; thus, the main focus of research was the aggregates of the cyan imaging dye. The cyan dye aggregates showed a bathochromic shift and a reduction in extinction coefficient. Both properties allowed more light to pass through to the red-sensitizing dye on the silver halide grains of the red layer and considerably enhanced sensitivity. The barium dye aggregates were destroyed in the bleach bath, such that the original cyan azo dye with high extinction coefficient and the required spectral absorption was set free.[23]

5. The coating process

Silver halide as well as photo-grade inkjet (IJ) media are multilayer assemblies that have to be made in a highly efficient, automated and very precise production process with high yield. High speed multilayer cascade or curtain coating of liquid layer assemblies was the process of choice of all manufacturers. It is a contact-free and premetered coating process, which produces nearly defect-free layers at high speed.[7] It can achieve uniformity along the coating width of less than 1% variation at coating speeds of more than 200 m/min for photo and IJ media. Experienced and skilled employees, good preparation, cleanliness and careful planning as well as optimized chemistry and process technology are needed to master this technology with high coating yield. Some of the photographic coatings plants that manufactured silver halide papers in the 1980s and 1990s were converted to produce photo-quality glossy inkjet papers in a similar process and on a similar base substrate. Instead of coating a photographic light-sensitive multilayer system, they coated polymer or nanoporous ink-receiving layers.

[23] R. Steiger and M. Schellenberg, Photografisches Material für das Silberfarbbleichverfahren. EP 0233152, 06.02.1987 (granted patent).

The ink-receiving layers absorb the ink vehicle, keep the colorant at the surface and provide a glossy or semi-matt finish. Figure 2 shows a schematic diagram of a typical multilayer coating process as it used for silver halide and photo-quality inkjet paper production.

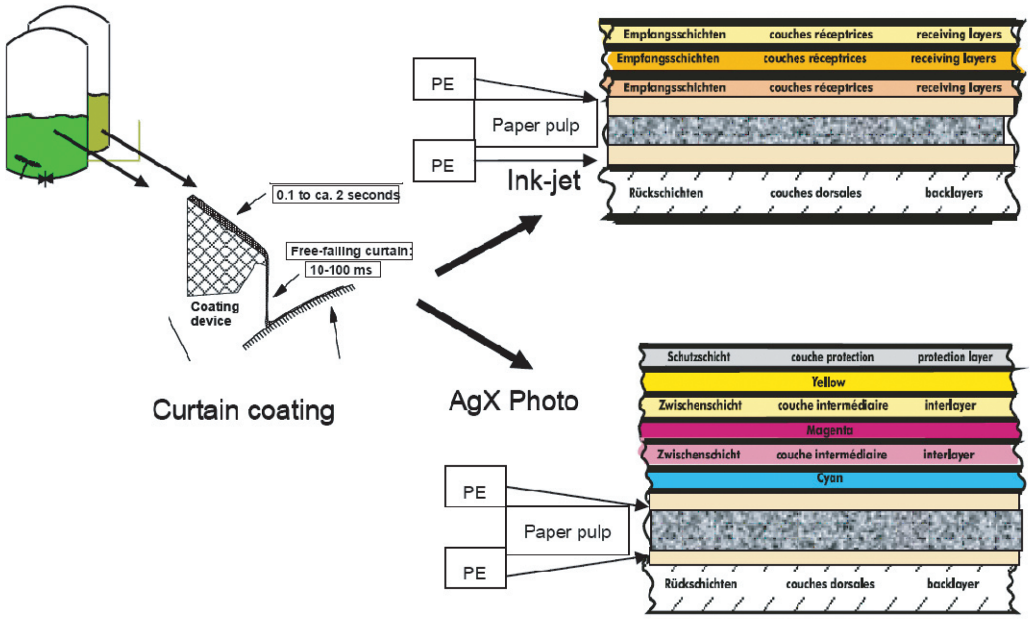


Figure 2. Curtain coating manufacturing process.

6. Surface modified titania in photographic substrates

Microporous particles of titania in either the anatase or the rutile modification have strong optical scattering properties and are frequently used as whitening agents. Titania is added as a whitener to the polyethylene used in the extrusion process of RC paper manufacturing. Around 1970, RC papers were first used as base substrates for silver halide papers. They suffered from severe cracking when framed and on display after rather a short time. It has taken years to understand the cause of the "RC cracking", which was finally identified as the destruction of the extruded polyethylene layer by reactive oxygen species that were created upon light exposure of the titania.[24] Both modifications of titania have catalytic activity under UV light which causes binder degradation in display media. The photocatalytic coefficient of anatase is ten times higher than that of rutile[25] and coating reduces this activity by another factor of 10.

Coated or core shell TiO_2 is made by adding a layer of a few nanometers of SiO_2 in the flame pyrolysis process.[26] This is the only type of titania used today by responsible

24 S. Wagner, An update of the stability of B&W resin coated papers. Washington, DC: American Institute for Conservation of Historic and Artistic works. *Topics in Photographic Preservation* **8** (1999) 60–66.
25 G. Wypych, *Handbook of Material Weathering*, 3rd edn. Toronto, Canada: Chem Tec Publishing, 2003.
26 P. Brandl, Evolution and regulatory impact of fumed inorganic materials in toners. *Proc. 24th Conf. on Non-Impact Printing*, (NIP 24), p. 1. Pittsburgh, 2008.

manufacturers of display media, be it silver halide or inkjet. No reports of cracking of the polyethylene layer with this type of whitener are known today. Nevertheless, the cracking of early RC papers has tarnished the reputation of this kind of paper with artists, museums and archives, which still prefer baryta as an archival base.

7. High quality inkjet papers

Different types of papers are used by artists and photographers for inkjet colour output from digital files.[27] The matt papers resemble traditional fine art papers with a visible paper structure and with a white matte coating of particles in the 1–5 micrometre range often on a textured base paper stock. These papers are made in paper factories with typical papermaking processes[28] and sometimes are coated with a matt mineral layer in a second step. As mentioned before, photo-like inkjet papers have a receiving layer coated on extruded RC paper stock, which gives them the look and feel and a construction very similar to those attributes of silver halide prints.[13, 29]

8. Requirements for inkjet receiving layer particles

Photographic look requires the print to have an optical colour density above 2 and high gloss. To achieve high optical colour density of the printed colorant, it must be fixed on top of the layer or—if it penetrates—the receiving layer must be highly transparent.[13, 14] High gloss requires a surface roughness of the receiving layer on a scale of less than 100 nm and a high gloss base substrate such as RC base. For high transparency, particles and the corresponding pores that make up the receiving layer should be well below the visible wavelength of light, best below 40 nm diameter, preferably with a narrow size distribution around 20–30 nm. Most importantly, the receiving layer has to be free of particles above 70 nm, which contribute to the scatter of light and turbidity and, subsequently, a reduction in colour density. If the particles are too small, the porosity becomes too low and ink absorption speed is slow.

In the inkjet industry, the pores of inkjet-receiving layers of a size around 20–30 nm are often called nanopores, referring to their physical size and discriminating them from the particles used in matte-coated paper, which are several micrometres in size. This is not in agreement with ISO standard 9277, which describes the method to determine specific surface area.[30] According to ISO 9277 such pores have to be referred to as mesopores (defined by a pore size of 2–50 nm) intermediate between macropores (> 50 nm) and micropores (< 2 nm). However, the term mesopores has never been adopted by the inkjet industry. This article will continue to use the term nanoporous as is common in the inkjet community for transparent porous receiving layers.

For nanoporous inkjet receiving layers, fumed mineral oxides of silica, alumina or boehmite, (AlOOH) are preferred to precipitated oxides,[31] as they have larger porosity at a

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27 http://www.imagepermanenceinstitute.org, and www.graphicsatlas.org
28 A. Kronherr, P. Achatz and G. Drexler, Nano-hybrid technology—A new tool for improving print quality. *Proc. 25th Conf. on Non-Impact Printing*, p. 536. Louisville, Kentucky, 2009.
29 A. Lavery and H. Siegers, Photomedia for digital minilabs. *Proc. 18th Conf. on Non-Impact Printing*, p. 494. San Diego, California, 2002.
30 ISO 9277:2010—The determination of the specific surface of solids by gas adsorption: BET-Method.
31 K. Fukunaga, K. Ishizu and H. Yamashiat, Silica filler for inkjet paper. *Proc. 17th Conf. on Non-Impact Printing*, p. 137. Fort Lauderdale, Florida, 2001.

similar surface area.[32] Fumed oxides are available in big bag quantities as powders with primary particle sizes around 20 nm, high surface area between 200–300 m^2/g, high purity, and different porosities and surface modifications. The nanopowders made of agglomerates need to be redispersed to their primary particles by liquid milling and dispersion for the coating process.[33] To form a stable receiving layer with enough mechanical strength for normal handling, bending, printer transport and post-lamination, a film-former and a hardener are needed. As a film-former, 10–15% of polymer binder—often a form of polyvinyl alcohol—is added to the diluted dispersion, as hardener mostly boric acid is used. This coating liquid is applied in a laminar flow process to the substrate (see Fig. 2) forming a stable film on the substrate upon drying and hardening. The evaporation of water creates a capillary porous nanostructured receiving layer, in which the air-filled capillaries with 20–50 nm pore size make up most of the volume of the layer.

The receiving layer is typically a mixture of 20% mineral oxide particles and 80% air. The pores are connected and open to the atmosphere, so that the ink can penetrate into the capillaries by expelling the air.[34] Interestingly, these porous receiving layers exhibit optical properties in between those of glass and air. Silica nanoporous layers with a refractive index < 1.15 have been achieved. Thin multilayers of such low indices can serve as low-cost antireflective films or light guides on polyester.[35] A scanning electron microscopic top view of the nanoporous silica layer of a glossy ILFORD Imaging inkjet paper is shown in Fig. 3.

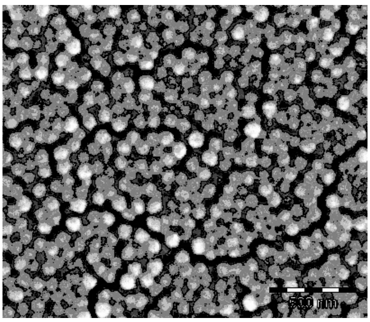

Figure 3. Scanning electron micrograph (top view) of a nanoporous layer. Scale bar represents 500 nm.

An inkjet receiving layer has to take up the full volume of ink needed to achieve a colour density of more than 2. With a typical colorant concentration between 5–10% in inkjet ink, this adds up to a volume of 25–30 mL/m^2 of liquid for the three colours. A mineral oxide matrix of about 25 g/m^2 of silica or—due to its lower porosity—of about 50 g/m^2 of alumina will provide enough pore volume.[36,37]

32 M. Withiam, Silica pigment porosity effects on color inkjet printability. *Proc. 12th Conf. on Non-Impact Printing*, p. 409. San Antonio, Texas, 1996.
33 Industry information II-2243. Products for the paper and film industry, www.evonik.com
34 K. Hornig and C. Schönfeld, High speed ink absorption using microporous RC based photo media. *Proc. 25th Conf. on Non-Impact Printing*, p. 547. Louisville, Kentucky, 2009.
35 G. Wicht, R. Ferrini, S. Schüttel and L. Zuppiroli, Nanoporous films with low refractive index for large surface broad-band anti-reflective coatings. *Macromol. Mater. Engng* **295** (2010) 628–636.
36 U. Fürholz, V. Ruffieux and M. Schär, Silica nanoporous dispersion and IJ layer. EP 1.655348 (2004).
37 P.-A. Brugger, J. Ketterer, R. Steiger and F. Zbinden, Aluminium nanoporous dispersion and inkjet layer. German patent 69700228 (1997).

9. Nanoporous receiving layer performance

The receiving layer has two main functions: absorption of ink liquid during printing, and the support of the image colorants once dried. Firstly, during the printing process it has to absorb the ink liquid fast enough such that the following drop does not hit the previous drop while it is still wet on the surface. The fastest inkjet printers (continuous mode) have a maximum drop frequency of 1 Mhz, but more typical are maximum jet frequencies of 40–50 kHz. Spreading of a drop takes place in microseconds and absorption in milliseconds.[38] The liquid (mostly water) will later evaporate out of the receiving layer over a period of hours when exposed to the environment. As can be expected from microfluid dynamics, nanoporous receiving layers with smaller capillaries do not absorb liquid as fast as microporous receiving layers, but are still fast enough for the fastest multipass printers today. Receiving layers composed of swelling polymer were popular in the early years of inkjet printing. However due to their absorption of water by a diffusion process, their ink uptake is much slower and printers have to be slowed down when printing onto swelling receiving layers.

The second function of the receiving layer is to maintain the colorants near the surface after drying. Inkjet dyes typically have a size of several nanometres and penetrate into the polymer matrix or the mineral oxide matrix, having pores of several tens of nanometres. The treated surfaces inside the pores are designed to fix colorants near the top of the layer.

Colour pigments used in pigment inks have an average diameter of about 50–200 nm and do not penetrate into a polymer or nanoporous receiving layer. There are several methods for fixing pigment inks on the layer.[39] In aqueous pigment ink, a small amount of polymer binder[40] helps to fix the colour pigments on the surface where they form a thin film (< 500 nm). The film of colorant and binder, sometimes called "cake", can considerably reduce the absorption speed for subsequent ink drops by clogging the pores.[41] The final thin film of pigment formed on top of the receiving layer is also prone to abrasion during printing while wet and when dry. When frequent handling of prints is part of the application as in consumer photos an additional clear film is applied over the dried colour layer. Microscopic cross-sections of nanoporous layers printed with dye and pigment are shown in Figure 4a and b, respectively.

Colour photo prints are supposed to last for more than a century in the dark and for several tens of years on display. To achieve this permanence the nanoporous matrix that makes up the receiving layer has to be inert and not show any catalytic activity and the dyes/pigments have to be of high permanence. Starting from a very low level of permanence (less than a few years) in the early 2000s, great progress was made in layer matrix and colorant design and ink formulation. Current pigment prints are claimed to last for hundreds of years.[42] The remaining

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38 G. Desie, S. Allaman, O. Lievens, K. Anthonissen and A. Sourcemarianadin, Influence of substrate printing in drop-on-demand printing. *Proc. 18th Conf. on Non-Impact Printing*, p. 360. San Diego, California, 2002.

39 S. Magdassi, The Chemistry of Ink-Jet Inks. Singapore World Scientific, 2010.

40 A. Shakhnovich, J. Carroll and D. Williams, Polymeric dispersions with specific affinity to pigments fir inkjet applications. *Proc. 25th Conf. on Non-Impact Printing*, p. 270. Louisville, Kentucky, 2009.

41 G. Desie, G. Deroover, F. De Voeght and R. Claes, Fundamental mechanisms in ink media interactions for aqueous, UV-Curing, and solvent based inks. *Proc. 20th Conf. on Non-Impact Printing*, p. 774. Salt Lake City, Utah, 2004.

42 http://www.wilhelm-research.com/

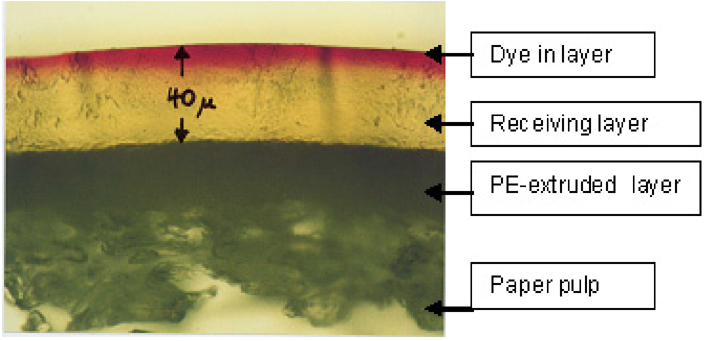

Figure 4a. Microscopic cross-section of a nanoporous inkjet (IJ) layer printed with red dye.

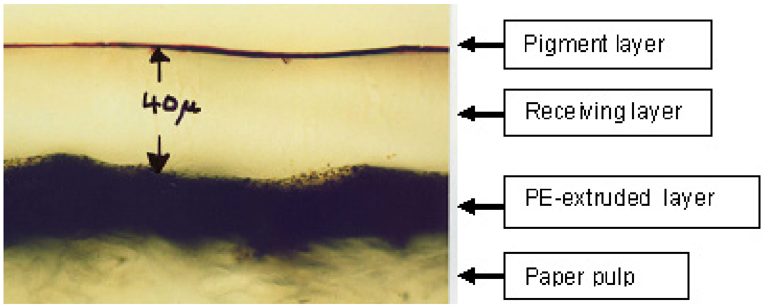

Figure 4b. Microscopic cross-section of a nanoporous inkjet (IJ) layer printed with pigment.

degradation of colorants seen with unprotected prints on nanoporous receiving layers is mainly due to direct attack of oxidizing gases on the finely dispersed colorants. Pollutants such as ozone, NO_x or SO_x have been found to cause premature fading.[43–45] Museums are used to keeping photographs in cool to cold storage.[22] However, inkjet nanoporous prints should, most importantly, be protected from pollution, for example by archival enclosures and filtered air.

10. Mineral oxide dispersion design

The key element of the nanoporous IJ receiving layers are fumed mineral oxides with a very high surface area. Boehmite and silica, commercially available in large quantities, are most often used. The surface chemistry of the powders and the dispersions is very important for forming a film upon drying and later a stable layer. While premade dispersions are available from mineral oxide manufacturers, they often do not have the right surface properties for the coating and film-forming process. Many inkjet paper coaters develop their own dispersions

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[43] *A Consumer Guide to Traditional and Digital Print Stability*. Image Permanence Institute, 2003. http://www.rit.edu/ipi/sub_pages/consumerguide.pdf

[44] D. Bugner et al., Ozone concentration effects on the dark fade of ink jet photographic print. *J. Imaging Sci. Technol.* **49** (2005) 317–325.

[45] J. Reber and R. Hofmann, Correlation of ozone test chamber data with real life permanence of inkjet prints. *Proc. 22nd Intl Conf. on Digital Printing Technologies*, pp. 231–234. Denver, Colorado, 2006.

from powders.[14, 46] Inorganic (e.g., aluminum chlorohydrate) surface treatments as well as organic treatments with aminosilanes are used. In the latter method, silanol groups of aminosilane react with surface silanol groups of SiO_2 to form siloxane bridges [(SiO_2)–Si-O-Si-(aminosilane) amino groups] that act as charge carriers below their pK_a of 9 and allow a very wide pH window. An acid is needed to protonate (charge) the amino group. A rather low treatment level is sufficient to stabilize the dispersion. Inorganic/organic aluminium–aminosilane complexes are used as surface modifiers as well as organic cationic polymers. The specific treatment has a very large influence on the rheological and film forming properties, but also on the permanence properties of the layer. Certain types of treatment absorb environmental pollutants and promote yellowing of the layer.[47]

Silica powder is a modifier of rheology. Balancing the right rheological properties and the gelling kinetics for a fast continuous coating process (up to 200 m/min) is an important part of the manufacturing recipe. On the one hand, a continuous coating process from a large premixed vessel requires long pot life. On the other hand, very fast setting of the layer is required once coated because of the high coating speed. For a continuous production process that may run for weeks in a row, manufacturing and maturing the nanoporous dispersion has to be completed in less than the typical coating vessel batch time of 6 hours. Bearing in mind all the requirements for coating quality and final performance it is not surprising that the development of a new dispersion that fulfilled all requirements could take up to two years of research, starting from commercially available fumed silica to an industrialized coating process. Because of the importance of the surface treatment and its sensitivity to the particular manufacturing process, many of the inkjet photo paper manufacturers preferred to develop a specific dispersion.

11. Analytical tools

The fast progress in the development of high quality photo-like inkjet media and inks was made possible by the availability of powerful analytical tools. Microscopy, electron microscopy, scanning ion micrography, X-ray diffraction (XRD) and other high-resolution imaging methods used to characterize photo emulsions have also helped to understand the structures, compositions and crystal morphologies of mineral oxide layers and their compounds. Atomic force microscopy (AFM) added the possibility to look at surface roughness[35] and detailed surface structure.

The analysis of dispersion and inks with disc centrifuges, sedimentation analysers and accoustophoresis reveals particle size distributions, zeta potentials and surface properties of particles in dispersions, coating liquids and inks. Static and dynamic wetting properties are of the utmost importance for the manufacturing process of the layer as well as for the jetting and absorption of inks.[39, 48, 49] Ink head and print engine designs are optimized by simulation of their

[46] P.A. Brugger, M. Staiger, R. Steiger, K. Peternell and O. Cohu, Nanoporous photorealistic materials for ink-jet. *Proc. 17th Intl Conf. on Digital Printing Technologies*, p. 411. Fort Lauderdale, Florida, 2001.

[47] J. Reber, R. Hofmann, M. Pauchard and U. Fuerholz, Spectrocopic investigation of IJ layer yellowing. *Proc. 23rd Intl Conf. on Digital Printing Technologies*, p. 711. Anchorage, Alaska, 2007.

[48] G. Wolansky and A Marmur, Apparent contact angles on rough surfaces, the Wenzle equation revisited. *Colloids Surf. A* **156** (1999) 381–388.

[49] A. Marmur, Wettability characterization of printing substrates: facts and interpretation, *Proc. 17th Intl Conf. on Digital Printing Technologies*, p. 129. Fort Lauderdale, Florida, 2001.

fluid dynamics.[50] The electronic waveform that controls the ink drop forming process is optimized by visualization tools that analyse drop speed and size, flight path and satellite formation.[51]

While it is possible to determine the bulk structure of nanoporous layers, it is very difficult to analyse the exact chemical surface modification, which strongly influences the properties of the layer; for example, the tendency to yellowing and diffusion, light stability and ink absorption speed. Today, very advanced methods such as XPS or TOF-SIMS can identify the binding and composition of single molecular layers around nanoparticles. However, from this information on final surface layer composition it is not easy to reconstruct the process by which the surface was formed. As a finely-tuned particle surface treatment process represents a competitive advantage, it is carefully guarded as a trade secret by the dispersion and ink makers as well as the paper manufacturers.

12. Large-scale manufacturing and health and safety of nanoporous materials

Dealing with industrial quantities of very low specific density, dusty powders represents a logistic and a health and safety challenge by itself. Converting those powders into nanoporous dispersions adds to the complexity. Fumed silica has a powder density of 40 kg/m^3. In manufacturing, powders, particularly fine powders, pose challenges in dosing, mixing and for occupational health. Industrial quantities of such powders are supplied in big bags. A typical photo inkjet production lot size requires 5 tons of powder corresponding to 125 big bags of 1 m^3 volume.

Personal protective gear has to be worn by the workers to prevent them from coming into contact with or inhaling fine dust and nanoparticles. In Switzerland, ILFORD imaging pioneered the investigation of silica nanoparticles in a large-scale production environment. With the help of the Swiss Agency for Occupational Health (SUVA) who made extensive measurements with specially developed monitors for nanoparticles in the air around the manufacturing installations in 2006, critical manufacturing steps and exposure levels could be determined and the production procedures could be adapted accordingly. In 2008, the supply of large manufacturing lots of powders was changed to silo trucks. Three large storage silos were installed as intermediate reservoirs. By pumping the powders from silo truck to reservoir in a fully closed system any contact of people with the powders was avoided.

13. Ink colorants and their surface morphology

Ink jet inks for digital printing are either made of dyes or colour pigments. In general, inkjet colorant chromophores are chemically the same as those used in traditional printing. Colorants need to be of high purity to avoid contamination of the print nozzle.[52] Some inkjet dyes are purified textile or pen dyes, others are specifically made only for inkjet.[53] Low salt content of the dye is

[50] D. Barnett and M. McDonald, Evaluation and reduction of elevated height printing defects. *Proc. 30th Intl Conf. on Digital Printing Technologies*, p. 38. Philadelphia, 2014.

[51] W. Voit, I. Reinhold, W. Zapka, L. Belova and K. Rao, Utilization of industrial inkjet technology for the deposition of conductive polymers, functional oxides and CNTs. *Mater. Res. Soc. Symp. Proc.* **1340**, p. 1377. San Francisco, (2011).

[52] A.S. Diamond and D. Weiss, *Handbook of Imaging Materials*, 2nd edn, p. 569. New York: Marcel Dekker (2002).

[53] K. Bättig and G. Jan, Magenta dyes for ink-jet printing. German patent 69605156 (1995).

important, as a high salt content compromises solubility. Precipitation of ink components affects the wetting in the print head channels; drying at the nozzle exit and may provoke nozzle clogging.

The market for colour pigments used in digital printing is less than 10% of the overall colour pigment market, which does not justify the synthesis of dedicated "digital" pigments. For example, carbon black dispersions and phthalocyanin pigments are used for black and cyan in ink jet as well as traditional printing. In general, inkjet pigments have to be of higher purity and of smaller grain size than traditional printing pigments. The diameters of inkjet colour pigments for photo printing are generally between 50 and 200 nm, while those of traditional colour pigments are around 0.5–2 μm. Traditional and inkjet pigments undergo a different surface treatment [54] as the ink formulation and printing requirements are very different from the two print methods.

Typical inkjet nozzle sizes are 10–20 μm in diameter. A study from the University of Sheffield showed that pigments as big as 5–7 μm—which was 1/3 the diameter of the nozzle—could be jetted.[55] However, the general rule of thumb is that the orifice diameter should be 100 times larger than the particle diameter.

Not only physical size but also rheological properties determine the best grain size for a particular pigment in specific ink. The sedimentation speed of a particle depends on the particle radius, the pigment specific mass and the ink viscosity. The ink-jetting process requires a low viscosity, below 30 cP for the ink. To stay buoyant in the ink for extended periods of time, particles need to be small. The higher the specific mass the smaller they need to be. For organic pigments, a size below 300 nm is generally stable against settling; the particle size of typical indoor inkjet inks is often in the range of 50–80 nm.

Inorganic pigments have a higher specific mass than organic pigments. Inorganic pigment dispersions have a strong tendency to settle and are maintained in an ink shaker in the printer.[56] Reduced sedimentation of particles in dispersion inks is achieved by fine-tuning surface treatment and particle size and ink viscosity.

Another advantage of smaller colour pigments is their higher colour brilliance;[57] their disadvantage is lower light stability. Milling down pigments to a tenth of their size may reduce their life expectancy as defined by ref. 58 by up to 50%. Such trade-off of light permanence against colour brilliance is only permitted for indoor use.

Pigment manufacturers and ink formulators have used an impressive range of surface treatments to keep small pigment particles in suspension and avoid agglomeration even over years.

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54 R. Baur and H.-T. Macholldt, High performance magentas for NIP applications. *Proc. 17th Intl Conf. on Digital Printing Technologies*, p. 842. Fort Lauderdale, Florida, 2001.

55 S. Hoath et al., Jetting complex fluids containing pigments and resins. *Proc. 30th Intl Conf. on Digital Printing Technologies*, p. 30. Philadelphia, 2014.

56 J.R. Barrit, W.R. Kaimouz, O.J.X. Morel, J. Tardrew and R.A. Wilkinson, Industrial digital manufacturing: Myth, hype or reality? *30th Intl Conf. on Digital Printing Technologies*. Philadelphia, 2014.

57 J.R. Castrejon-Pita, W.R.S. Baxter, J. Morgan, S. Temple, G.D. Martin and I.M. Hutchings, Future, opportunities and challenges of ink-jet technology. *Atomization Sprays* **23** (2013) 571–595.

58 D.E. Bugner and P. Artz, A comparison of the image stability of digital photographic prints produced by various desktop output technologies. *Proc. 18th Intl Conf. on Digital Printing Technologies*, p. 306. San Diego, California, 2002.

Special dispersants, encapsulation, attaching functional groups, diazonium treatment, coupling and crystal modification are some of the techniques used for surface chemistry in colour pigments.[59] Not only agglomeration but also the final permanence of pigments strongly depends on the specific surface morphology. Some yellow pigments are challenging to surface-treat and stabilize.[60] In a number of inkjet printers on the market, yellow is by far the least light-permanent channel in typical daylight exposure. For prints made with those printers, additional UV filtering is highly recommended when on display.

The intricate fine-tuning of ink dispersion stability, reliable jetting, adhesion on the receiving layer and long-term print stability is one reason why the formulation of pigment inkjet inks requires considerable know-how and is mastered by rather few companies. More than the compounds used in the formulation it is the surface treatment of the pigments that constitutes the essential process know-how of pigment and ink manufacturers. Chemical companies do provide ready-made colorant dispersions for generic ink formulations, but they do not suit for all applications.

14. Summary

Surfaces provide much of the functionality of silver halide and ink jet photographic media and colorants. Colloid chemistry, dispersion milling and surface treatment processes have constituted key know-how for photo media manufacturers from the early 20th century to today. The exact chemical surface composition and particularly the process of treating the surface reproducibly are difficult to reverse engineer and constitute a major piece of manufacturer's proprietary knowledge and competitive advantage, which they keep as trade secrets. Even if only a few nanometres thick, the layers around silver halide grains, mineral oxide particles or colour pigments play a major role in the manufacturing process and in the performance of the final print.

Acknowledgment

The move to digital inkjet papers and progress in technology at ILFORD has only been possible because media designers, organic chemist, analytical chemists, physicists and engineers worked together as a motivated, multidisciplinary international team. I am thankful to all my colleagues in R&D in Marly and Mobberley (England) who made the more than 25 years of the digital evolution from analogue photo to digital photo and inkjet at ILFORD such an exciting experience.

[59] www.cabotcorp.com/.../inkjet-colorants/whitepaper
[60] A. Shakhnovich, New inkjet yellow pigments—halogenated quinolonoquinolones. *Proc. 25th Non-Impact Conf.*, p. 276. Louisville, Kentucky, 2009.