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New Chemistry in the Digital Darkroom

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Abstract: A state of the art and successful industrial application of nanoparticles, digital ink-jet photo paper, is presented. The new photo paper replaces the traditional barite papers in the reproduction of art and high-quality black and white prints. The patented process takes place at the interface of chemistry and physics. Individual steps are briefly explained.

Keywords: Art paper · Digital ink-jet photo paper · Nanoparticles · Titanium dioxide

Introduction

Nowadays it is well accepted that the first and most successful industrial application of nanoparticles is modern digital ink-jet photo paper. Well-known companies such as Ilford, Oji, Felix Schöller or Mistubishi Papers have made large investments in many years of development and stacks of equipment for the mass market production of microporous ink-jet photo paper. Compared to the few other industrially successful applications of nanoparticles, such as silver nanoparticles in antibacterial coatings, modified textiles and easy-to-clean surfaces, photo paper is still the major playground for the game of the small nanoparticles.

Aside from the main bulk of photo paper however, a few smaller companies have found some challenging projects waiting to be realised. The following example shows how a small player in a big market jumped on the bandwagon to modify the established product chemistry to offer new and astonishing possibilities hitherto unknown. This is an ink-jet paper for the reproduction of art and for the 'digital development' of black and white prints in a quality which was only achievable previously with analog darkroom barite paper. Until recently analog barite paper was still considered the best paper for deep black images, tuneable gradation and long lasting results. These advantages are however paid for with an incredibly demanding and unpleasant process in the dark room.

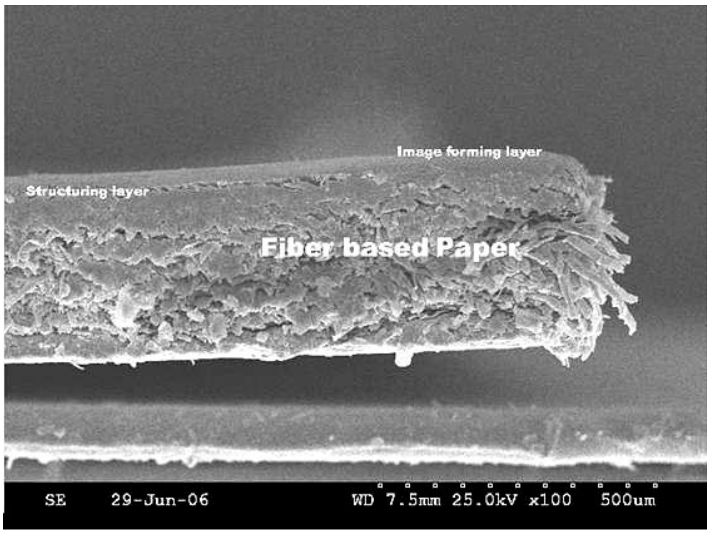

Fig. 1. Cut section of the new art paper. The paper fibres are visible.

Finding Paper and Coating

The chemistry of a nanoparticle formulation and a coating of such a mix are very complex and a lot of trial-and-error chemistry is still undertaken today. Microporous photo paper on polyethylene coextruded paper is currently available. This paper looks and feels quite similar to 'normal' photo paper. Digital art paper on the other hand has been produced for the past few years but only as matte paper for ink-jet applications. We took on the challenge to combine these products, using whatever chemistry necessary to achieve the goal of a glossy art paper for an optimal reproduction of photographic prints, especially for black and white images.

In the beginning was the right paper. Together with partners in the paper industry we found a suitable base paper rather quickly, a fibre-based open paper with a smooth texture (Fig. 1). The colour tint was given by stable titanium dioxide rather than barite, since the quality of titanium dioxide is nowadays at least as good as or maybe even better than classical barium sulphate in barite papers. We chose one version with and another without optical brightener in the paper to meet the different customer tastes for harder white or more natural white colours.

The second task was to develop the microporous ink-jet accepting coating. After three years of development we were able to find a new approach towards such a coating. Many or nearly all modern micropo-

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rous ink-jet coatings are very brittle. On a flexible fibre-based paper this would lead to the final product breaking and cracking much too easily. Furthermore the paper and image should not yellow under any circumstances; whether daily exposure to light or air. Lastly we worked out a formulation which leads to a dense black and very precise black gradation with the best ink-sets available.

The amount of time, money and equipment for such a trial-and-error development was at the borderline of affordability for a small company, but finally we got on top of the major demands and developed a feasible way to tune the chemistry to our needs.

Formulation of the Metal Oxide Nanoparticles

In the beginning was the choice of the right nanoparticle. It had to be chemically prepared and later dispersed to lead to a narrow particle distribution of around 100–120 nm in water. The main development and production of the particle itself was a costly process, carried out by one of the few worldwide producers in the field. Our part was the development of a suitable formulation and upscaling the process for mass production. In water-based metal oxide nanoparticle dispersion formulations the first mixing and dispersion process is very important. Measurements at EMPA Dübendorf during different steps of dispersion gave us the indication of the best equipment and chemical setup. We found out that particles larger than 200 nm drastically reduce the gloss of such a coating and should be avoided as far as possible. In Fig. 2 the dispersion steps that lead to an optimized, narrow distribution are shown.

As dispersing equipment we used a typical Rotor-Stator device as shown in Fig. 3.

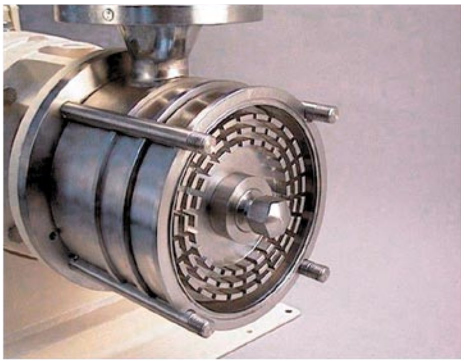

Fig. 3. Rotor-Stator Dispersion unit for dispersing nanoparticles to a narrow size distribution

To find the optimal geometry and setup, we checked the various possibilities at the real-size test laboratory of the manufacturer.

The amount and type of polymer binder to work with the nanoparticles in the formulation was defined to be as low in concentration as possible and as stable as possible when finally exposed to air and light. After screening several binder categories, we choose the rather simple and well known poly vinyl alcohol to be the best compromise. Since normal, standard poly vinyl alcohol is not suitable for our process, we were lucky to find a particular derivate of this polymer from one single supplier which offers perfect working attributes.

As it can easily be analysed, the proportion of pigment to binder in such a coating is in the range of 10:1 or even higher. Therefore these are no longer polymeric coatings, but nearly fully inorganic coatings, since in the dry state less than 10% of the coating is of polymeric nature.

Combining Coating and Paper

Finally having the tools together, we needed only to combine the paper and ink-jet layer to finalise the art paper. However here was one of the intrinsic difficulties of the project, the combination of a weakly basic to neutral, flexible, structured fibre-based paper with an acidic, inflexible, perfectly regular microporous coating.

To overcome these difficulties, we developed a specific barrier layer. The characteristics and ingredients are secret, but what it mainly does is to seal the paper surface with a pH-barrier. However that is only half of the truth, since it has two other features as well. We believe that during the application of the liquid microporous formulation onto the barrier layer, the clusters of oxidic nanoparticles in the dispersion start to aggregate on the surface, building a regular first layer whereupon other nanoparticles can quickly arrange to form a nearly crack-free but highly porous layer of 30–35 gr/m^2 of dry material in one production step.

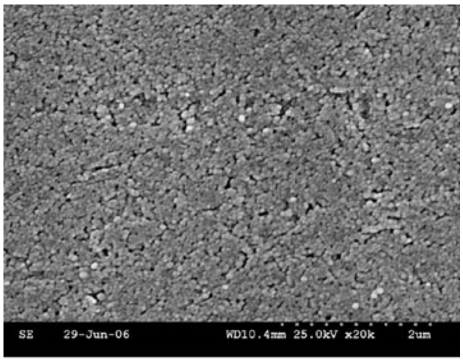

Fig. 4. Surface SEM of final microporous coating on fibre-based art paper in high resolution

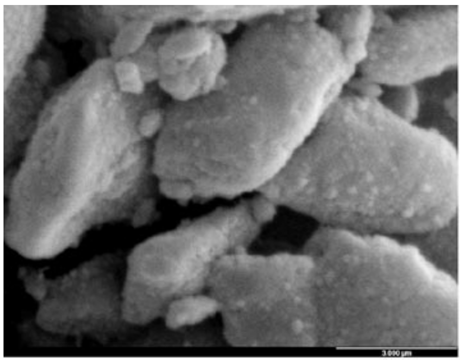

Fig. 5. Surface SEM of matte art paper in comparably high resolution

In comparison to the microporous coating shown in Fig. 4, Fig. 5 is a SEM picture of typical matte art paper under similar conditions.

Combining the glossy ink-jet coating with a fibre-based paper finally led to a viable product which was launched in 2006. It is in the meantime highly appreciated by photographers worldwide (Figs. 6 and 7) and was awarded the TIPA Award 2006 for the best independent Ink-Jet Paper. Several stability and ageing characteristics are still under investigation.

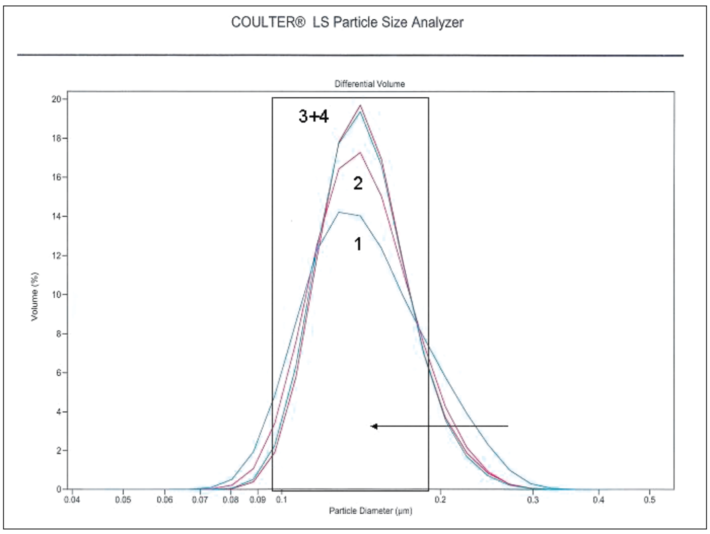

Fig. 2. Nanoparticle distribution in water, optimization of the dispersing process (from 1 to 4)

Fig. 6. Exposition Photokina 2006, American photographer Doug Menuez

Fig. 7. Exposition Photokina 2006, British photographer David Osborne

Conclusion

In combining a well-suited fibre-based paper with a modern nano-technology-based microporous ink-jet layer and a sophisticated barrier or intermediate layer, we have finally remapped modern chemistry into the digital darkroom. Up to now high-quality photographic art reproduction was undertaken with paper and chemistry based on 19th century technology, although camera technology has changed drastically. Using many kinds of different chemical raw materials and modern techniques, we have established a coated art paper of a new level that allows digital fine art images to be reproduced with rather simple equipment at home. All you need is a decent ink-jet printer (for example Epson R2400) and the right paper for the job.

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