Fixation of Pigmented Black Ink on Matte Coated Ink-Jet Substrates

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Abstract

Pigmented ink jet inks present a challenge to the developers of the ink-receptive media. Unlike dye-based ink jet inks, pigmented inks, especially black, suffer from color transfer and rub off. Black ink fixation problems are especially prevalent in large format printing used in CAD or architectural design.

This study focuses on the properties of the materials used in microporous coatings for ink jet media and how they impact the media's interaction with pigmented ink jet inks. Material properties such as pore volume and particle size are studied, also binder types, additives, and ratios such as pigment to binder ratio and the ratio between hydrophilic and hydrophobic binder materials. For print evaluation an HP Designjet 100+ was used and methods were developed to evaluate the quality of pigment ink fixation. SEM analysis and dynamic contact angle measurements were used to analyze ink-media interactions.

The study showed that the formation of an ink pigment filter cake on the coating surface correlated to poor black fixation and in contrast, when no filter cake exists the fixation is good. Good fixation results are achieved when the dynamics of ink absorption into the media coating prevent the formation of a pigment filter cake on the surface.

Introduction

We do not have to list the arguments for the use of pigmented inks in the practice of ink-jet printing, but often the fixation of the ink is not sufficient, especially black printed letters, areas and objects. The problem can be the transfer of the black to the opposite side when a sheet is folded, sheets are stacked or to the backside, when a poster is rolled up; but also the removal of black parts, when the surface undergoes a mechanical rubbing.

Our first approach to the problem was to modify the media surface in such a way that the ink particles are better bound. This approach addresses the situation in the "binding layer"; see the scheme below.

Studied parameters were pigment to binder ratio, different types of binders including materials with non-polar domains in the molecule, cationic and anionic charged receiver layers, lower and higher pH plus the addition of micronized wax particles. The latter could improve the rub problem to some degree. Overall no improvement could be achieved. This is not really surprising since any interaction between substrate and pigment particles can take place only to the first layer of pigment spheres! Everything above would have to be bound by a binder formulated into the ink, which is probably not present due to the requirements of ink stability, viscosity and the like.

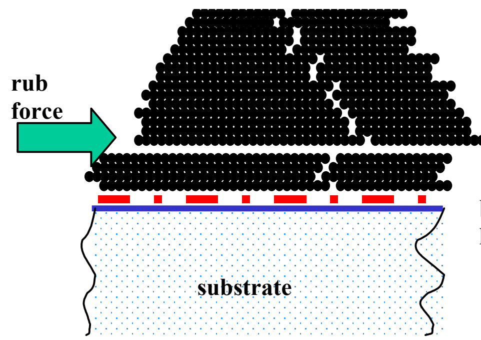

Figure 1. Black pigment particles on a substrate, schematic.

The conclusion was, for the prevention of the above listed fixation problems, a more geometrical approach was required; investigating the media surface structure.

Electron Microscope Studies

The surface of a number of printed substrates was evaluated by means of SEM.

For easier comparison we tried to capture the line between the unprinted media and a black printed square, in figure 2 and 3 on the right half of the picture.

On the right half of the picture figure 2, where the black printed area is, one can clearly see the silica surface covered with what looks like filter cake formed by the black ink particles, in the same way as M. Graindource had found it in his studies of pigmented inks printed on photo glossy substrates – see reference list. Such a filter cake was not present on a media with good black ink fixation properties as can be seen in the next picture.

Also from the cross section comparison, it is obvious that there is a substantial filter cake on the surface of the substrate with poor fixation properties see figure 4. The good media has little pigment particle coverage on the surface of the silica particles, the larger portion of pigment black had penetrated deeper between the silica of the coating.

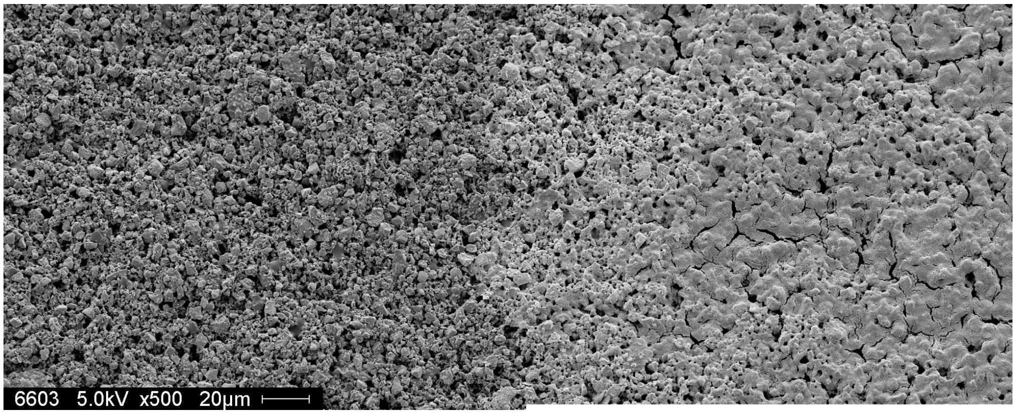

Figure 2. SEM picture indicating a filter cake on the surface in the right part of the picture which was printed

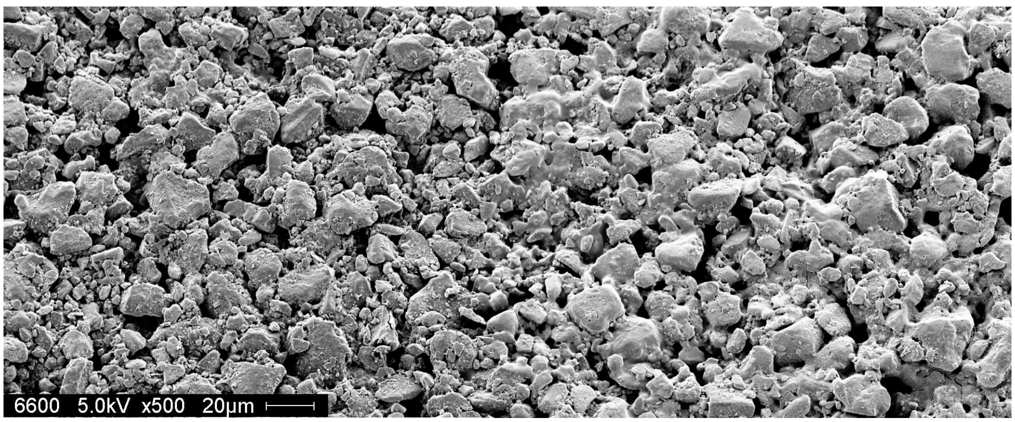

Figure 3. SEM picture from a surface with no black ink transfer problems

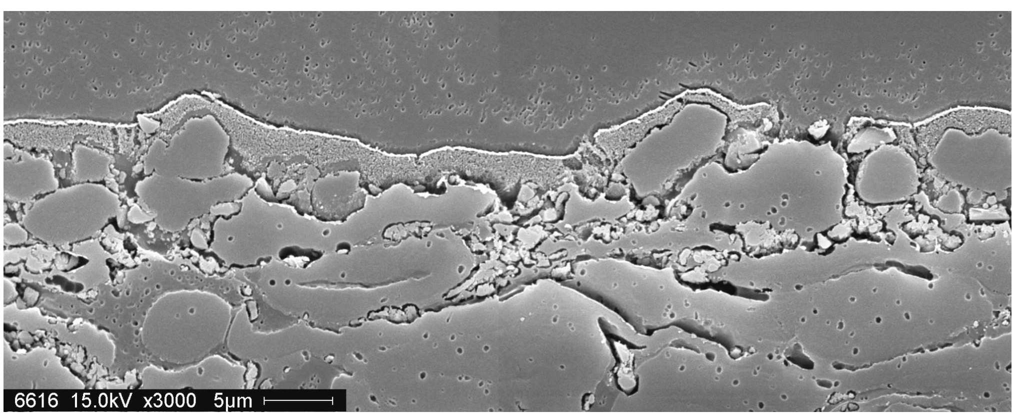

Figure 4. SEM picture from the cross sections of the first paper, figure 2 Above with filter cake

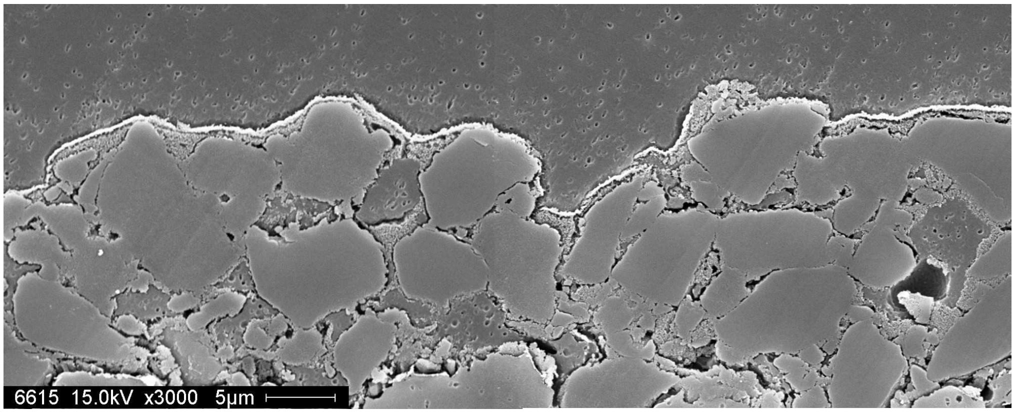

Figure 5. SEM picture from the cross section of the second paper above, indicating no filter cake formation

Automatically this leads to the question about the black saturation/optical density, when the ink particles go deeper in between the silica particles of the coating. From over 40 trials and comparison media, it can be said that there is not necessarily a negative correlation between densities and black transfer. It is possible to achieve highest black density together with good fixation.

Which parameters in the ink-receptive layer of the substrate are now responsible for the forming of a filter cake on the surface in one case and the preferred situation of a more uniform deeper penetration of the pigment particles inside the silica pigment coating?

Comparison of Black Pigment Particle Size Distribution with Silica Pigment Pore Diameter

The main material in matte ink receptive coatings is silica gel pigments with pores inside the particle and also a high internal surface area. This sponge like structure is ideal to absorb dye based ink molecules on the large internal surface, but can the black ink pigment penetrate inside the silica particle? Obviously not, the silica pores are too small, typical average pore diameter of industrial grades is between 15 and 25 nm.

Dynamic Contact Angle Measurements

The dynamics of liquid absorption into a porous substrate is controlled by capillary forces, surface tensions and polarity. We made measurements by dropping original black ink-jet ink onto the substrates and compared the level and dynamic changes of the contact angle. Even though real drops in an ink-jet printer are much smaller, maybe 3 to 30 pl compared to about 3 µl of the ones the instrument puts on the test media, the surface tension and the change over time will probably correlate to some degree with the printer situation. We found a strong correlation from these measurements with the fixation of the black.

According to surface tension theory a high contact angle stands for less spreading of the liquid and low surface tension. Low contact angle equates to faster spreading and higher surface tension. In case of a porous surface, the spreading is not only horizontical, but liquid is absorbed into the layer.

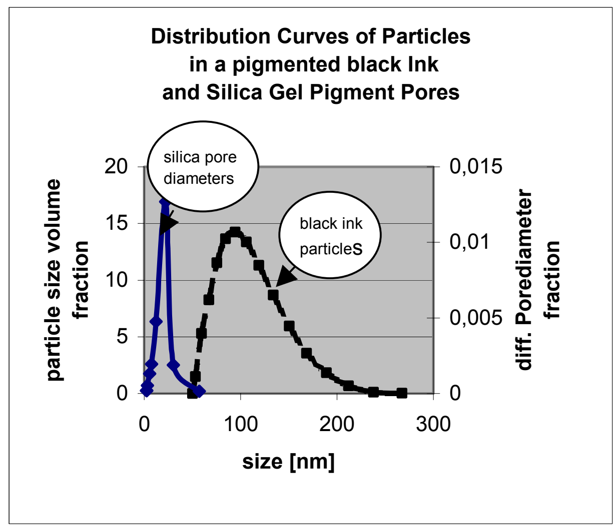

Figure 6. Distribution curves

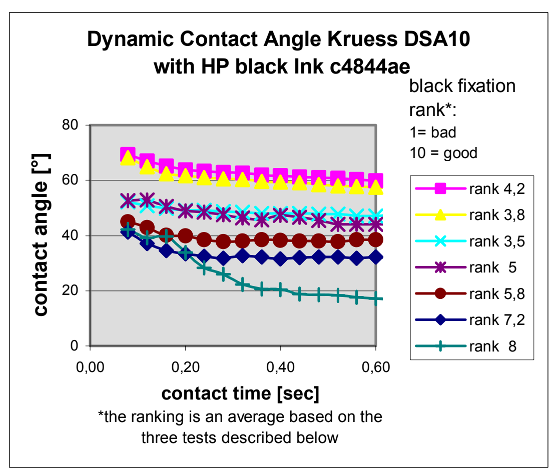

Figure 7. Dynamic contact angle measurements:

It may not be so simple to explain how the ink absorption really takes place, that at the end for a good media the pigment has penetrated, whereas for a poor media a filter cake is formed. For further evaluations and analysis, the contact angle reading after 0.52 seconds was used.

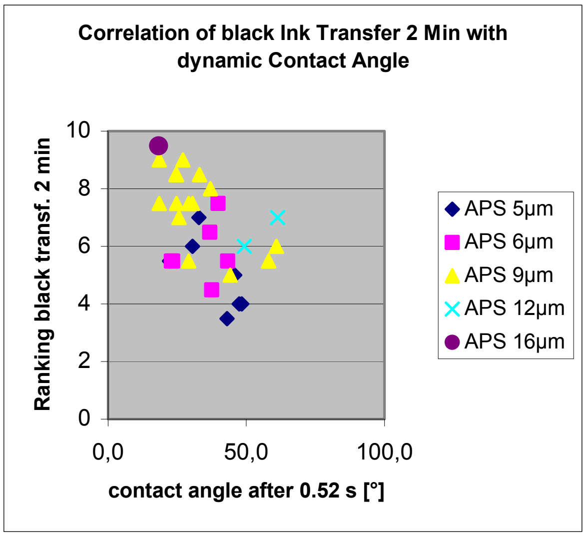

Figure 8. Correlation contact angle with black transfer. Ranking black transfer 2 min: 1 = poor, 10 = good

This graph shows a clear correlation with better results for lower contact angle readings! But also indicates an influence of the silica particle size and probably substantial variability.

Design Parameter for Receiver Layer Optimization

To study the situation further, a selection of factors, which define a receiver layer recipe, were varied in a lab series. Whereby a main target was to create a range of surface tension levels. This was addressed by the ratio of the two binders used in the recipe – polyvinylalcohol being hydrophilic and a dispersion binder – polyvinylacetate (Latex), more hydrophobic.

Experimental Factors:

PVOH / Latex ratio
Average particles size silica
Pore volume silica
Receiver layer coat weight

The design was D-optimal including terms for interactions between factors and squares to identify non linearities.

Main Results

Since it was an important target, to achieve different levels of the coating surface tension or a range from more hydrophilic to more hydrophobic character, this parameter was analyzed first. We found readings from about 20 to 60 °, measured as described above. It is interesting to see that the surface tension depends on all chosen factors and there are significant interactions, see figure 9. The strongest factor found was the PVOH / Latex ratio:

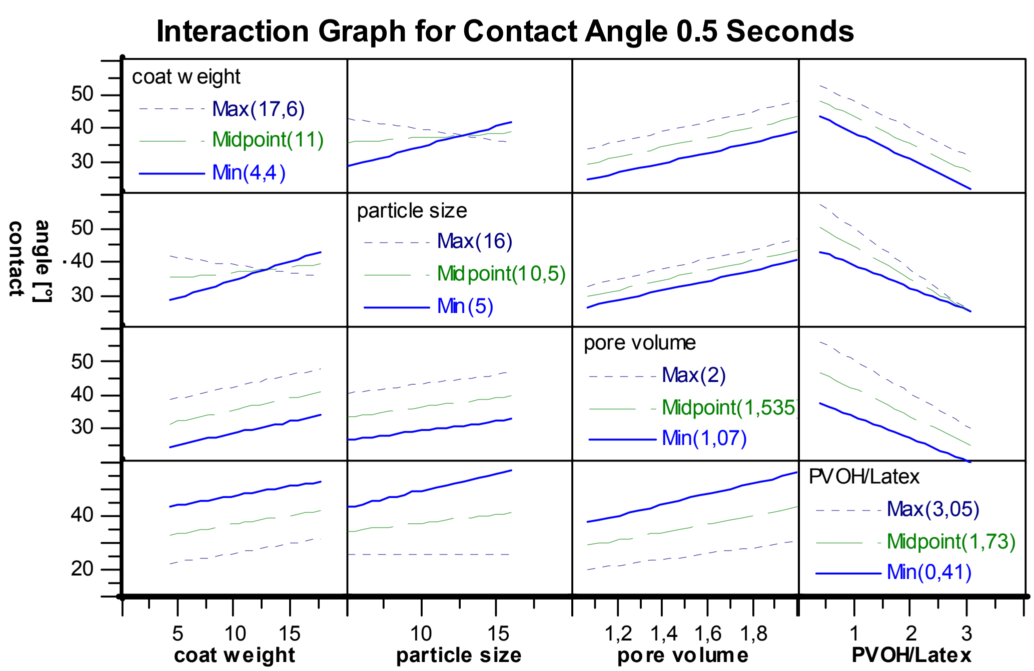

Figure 9. Interaction graph for the dynamic contact angle

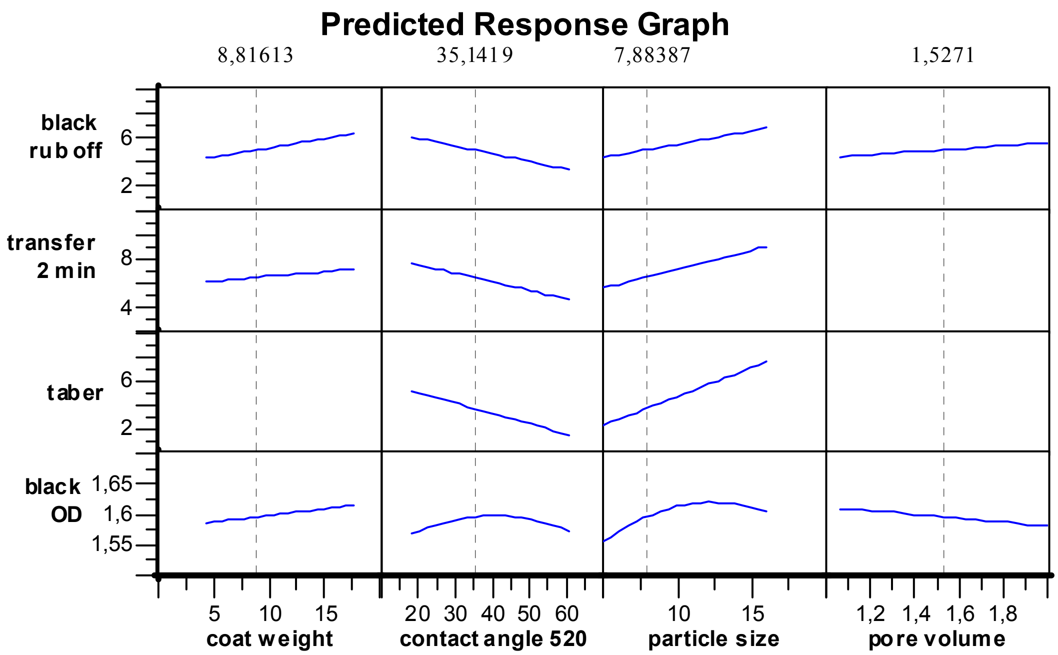

Figure 10. Predicted response graph

Figure 10 matrix graph now represents the main results after multiple regression including interaction terms.

Interpretations

The contact angle as created by the PVOH / Latex ratio together with other parameters, has a strong significance on the black fixation tests.

Larger silica particles have a beneficial effect on the black fixation–large particles create more inter particle voids allowing an easier absorption of the black pigment.

A higher coat weight is also helpful. The influence of pigment pore volume of the pigment on the investigated parameters is small, a slight reduction of the black density was found.

These findings provide indications in which direction a receiver layer could be optimized for better fixation of pigmented ink. This work related only to one printer and one type of pigmented ink, but even if other inks have different particle size, other surface tension, it is most likely that the formation of a filter cake on the substrate surface has to be avoided.

Experimental

Silica pigments used were Grace Davison SYLOJET® P 405, P 409, P 412, P 609, P 616, SYLOID® W 300, ED 3, 72. Polyvinylalcohol from Kurraray Mowiol® 23-88, the dispersion binder was Vinnacoat LL 4444 a polyvinylacetate from Wacker Chemie. Two cationic additives – SYLOJET® A 200 Grace Davison which is an aluminium salt and a polydadmac Induquat® 35 L from Indulor Chemie. The pigment to binder ratio was adjusted to the porevolume of the silica pigment. As substrate a 90 g paper made from chemical pulp with calcium carbonate filler and neutral sizing was chosen.

The labcoatings were printed on HP Designjet 100+ with the standard black ink C4844AE.

In the evaluation of black ink fixation three different methods were used:

1. Taber Abraser – the printed sheet was folded, so that plain coating surface did cover the black area. The package was put under the wheel and after 5 rotations the transfer onto the white surface was evaluated.
2. Transfer two minutes – the fresh printed sheet was dried for 2 minutes ambient, the sheet was folded like above, placed on a smooth rubber surface, then the 5 kg weight Cobb roll was moved 2 times over the package. Again the transfer of black was evaluated.
3. Black rub off – in this case no machine was used, but a stripe of white paper was moved over a black printed area under light pressure (with a "calibrated" finger) 10 times. The pick up of black ink on the white sheet was ranked. There are rubbing machines, which may do this in a more reliable way.

For 1 and 3, the print had time to dry under ambient over 24 hours.

The transfers were not very regular, density measurements and the like did not work, so all three tests were evaluated by a visual ranking, with always 1 = poor, 10 = very good, means no transfer.

Contact angle measurements with Kruess DSA 10, using original black ink which was taken from an ink cartridge HP c4844ae to form the drops.

References

1. D.M. Chapman, "Design considerations for Matte-Coated Microporous Media for Pigmented Inks" IS&T 19th proceedings pages 598-602.
2. Desie, Van Roost, Graindourze, De Keyzer - IS&T's 20th proceedings page 946 to 951.

Author Biography

Wolfgang Storbeck received his chemical engineer in 1973.

He started as technology engineer in the manufacturing of circuit boards at Grundig and coating of magnetic tapes for Agfa. Followed by 18 years in paper industries for Felix Schoeller in development and technology for photo base papers and later digital imaging media. This included raw base developments and coatings for ink-jet.

In 2001 he started in his present position at Grace Davison. He works in the digital medial group for technical customer service and in the application laboratory. Subject is mainly the use of pigments in ink-receptive and other coatings for print media.