

AEROSIL® Fumed Silica and AEROXIDE® Fumed Alumina for Glossy Photo Inkjet Media

Technical Information 1331



AEROSIL®

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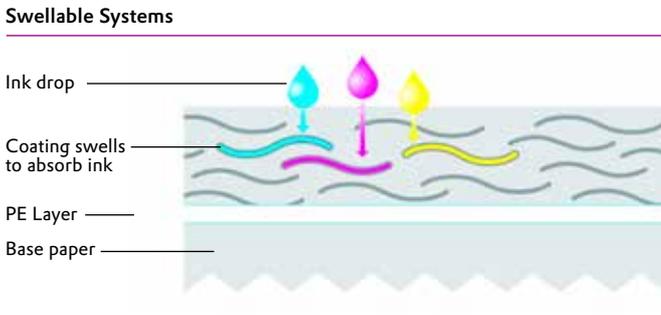
1 Introduction

1.1 Swellable Systems

Traditional polymer coatings absorb ink drops, and the dye molecules dissolved in them, by swelling up with liquid and then slowly drying again to lock in the dye. This process takes some time; consequently, the high speed of advanced inkjet printers may cause colors to run together and diminish the image quality. If the printed image is exposed to high humidity or water, the dyes can become re-mobilized, resulting in degradation of the image. Ultimately, these types of coatings are, for the most part, not water-resistant.

Many of today's inkjet printers not only print with dissolved dye molecules, but also with ultra-fine color pigments. These pigments are not able to penetrate into the polymer coating and remain on its surface, where they can be easily wiped off by touching. The difference in gloss between the shiny polymer surface and the deposited pigments is also very noticeable. For good quality results, swellable papers should only be used with non-pigmented inks and at the slowest printer settings. Photographs printed with dye based inks, however, tend to fade when exposed to light and air, resulting in a limited life span.

Figure 1.1 Traditional inkjet media based on pure polymer coatings adsorb the ink drops by swelling

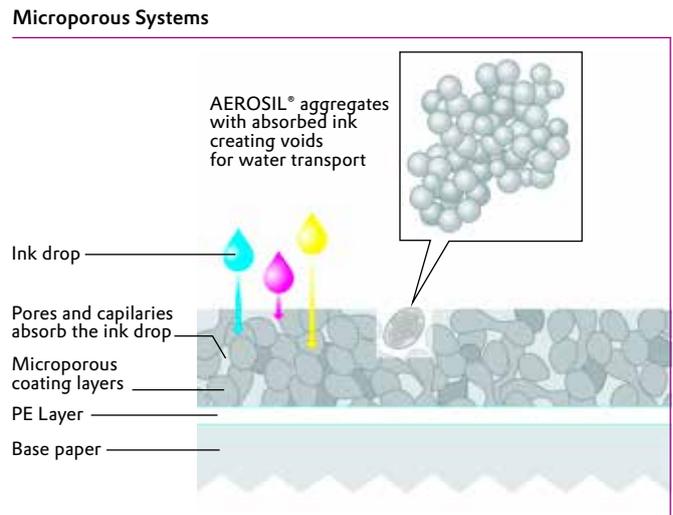


1.2 Microporous Systems

Microporous coatings consist of an inorganic "sponge" that has a well defined pore and channel structure. Because of their unique fractal structure, fumed metal oxides, such as AEROSIL® fumed silica and AEROXIDE® fumed alumina products, form this sponge with a minimum amount of polymeric binder. When an ink droplet hits the paper surface, the coating absorbs the liquid in a fraction of a second. This "instant dry" performance of microporous coatings enable the use of high speed printers while achieving optimum image quality.

The dyes are absorbed on the surface of the solid fumed metal oxide particles (which are called pigments within the paper industry) with pin-point accuracy. Capillaries carry away the water, resulting in both brilliant colors and high resolution. Since the negatively charged dyes adhere to the positively charged (cationic) particles electrostatically, additional liquid is unable to dislodge them. As a result, the images are water-resistant.

Figure 1.2 Microporous systems absorb liquids much faster than swellable coatings and are compatible with both dye and pigment-based inks.



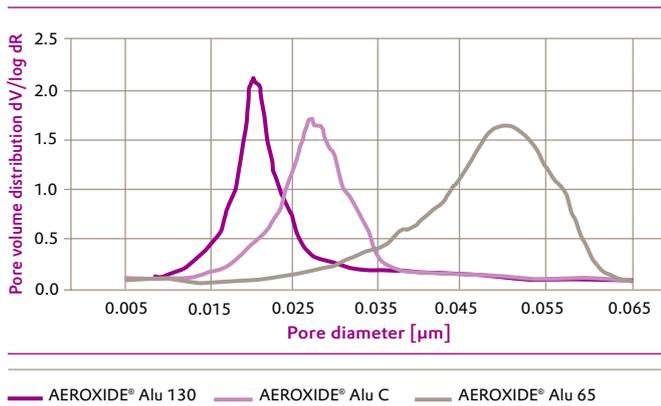
Microporous inkjet media are universally suitable for all types of ink. Their porous structure absorbs both dissolved dye molecules and dispersed pigments. The use of pigmented inks is increasing due to their high resistance to environmental conditions which substantially improves the lifetime of photo-inkjet prints. The extreme fine particles of AEROSIL® and AEROXIDE® products make them especially suitable for glossy coatings.

1.3 Special Properties of Microporous Inkjet Coatings

Mercury Intrusion Spectroscopy is a very good method for determining the size and volume of the pores of microporous inkjet media. **Figure 1.3**, for example, shows the pore size distribution of AEROXIDE® fumed alumina based microporous paper coatings. By choosing the correct AEROSIL® or AEROXIDE® grade, it is possible to customize the property profile of the finished paper.

Since the absorption of fluids is strongly determined by the PVD (pore volume distribution) it is wise to find the right pore sizes for the given IJ ink. Below the PVD of our series of aluminium oxides is shown. Due to their perfect PVD the products AEROXIDE® Alu 130 and Alu C lead to high performance coatings for aqueous IJ coatings. Our AEROSIL® range of pyrogenic silicas offer also an interesting range of PVD's. For photographic IJ coatings we recommend AEROSIL® 255 and AEROSIL® 300 for perfect results. Since the surface charge of silicas is anionic there is the need of modification which is shown later (p. 6).

Figure 1.3 Pore size distribution of fumed alumina based microporous paper coatings (from ref. 4)



The color brilliance of microporous coatings is based on the incorporation of the dyes and pigments into the coating, especially on its surface. Color brilliance is measured in terms of its "gamut," the area of an a^*b^* diagram that a particular inkjet printer can generate in combination with the microporous substrate (**Figure 1.4**).

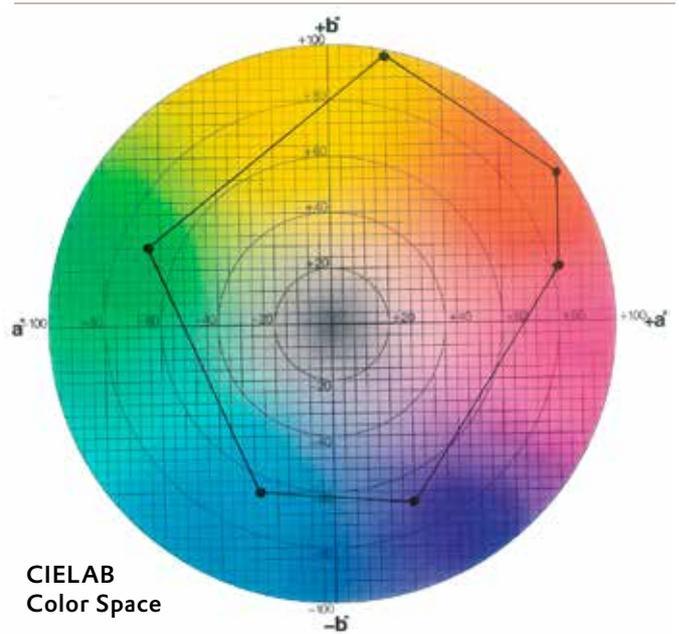
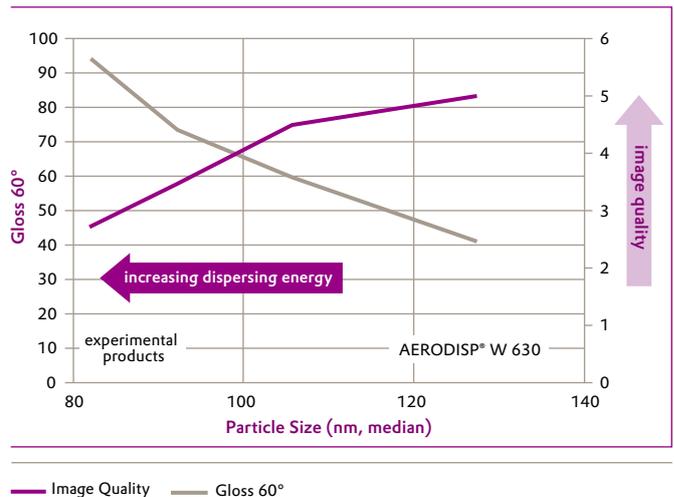


Figure 1.4 a^*b^* diagram as a measure for color brilliance

Microporous coatings based on AEROSIL® and AEROXIDE® particles typically feature gloss values between 30 and 50% (measured at an incidence angle of 60°). The gloss typically depends both on the average pigment aggregate size and the median coating pore diameter, increasing when both features become smaller. Image quality, on the other hand, suffers when the pores become too small because ink absorptivity is reduced. We have proved this by an experimental series based on our fumed alumina dispersion AERODISP® W 630 (ref. 3).

Figure 1.5 Impact of particle size on gloss and image quality



As shown in **Figure 1.5**, increased dispersing energy leads to smaller particle sizes. At the same time gloss increases while image quality is being degraded.

2 Manufacture and Properties of AEROSIL® and AEROXIDE®

The **water-fastness** of microporous coatings depends on the surface charge of the pigments as well as the binder. Cationic pigments, such as fumed alumina or cationized fumed silica as well as crosslinking a binder such as poly-vinyl alcohol (PVA), are essential to produce water-resistant papers. **Figure 1.6** shows the difference in terms of water-fastness between a paper coating produced without and with crosslinker.

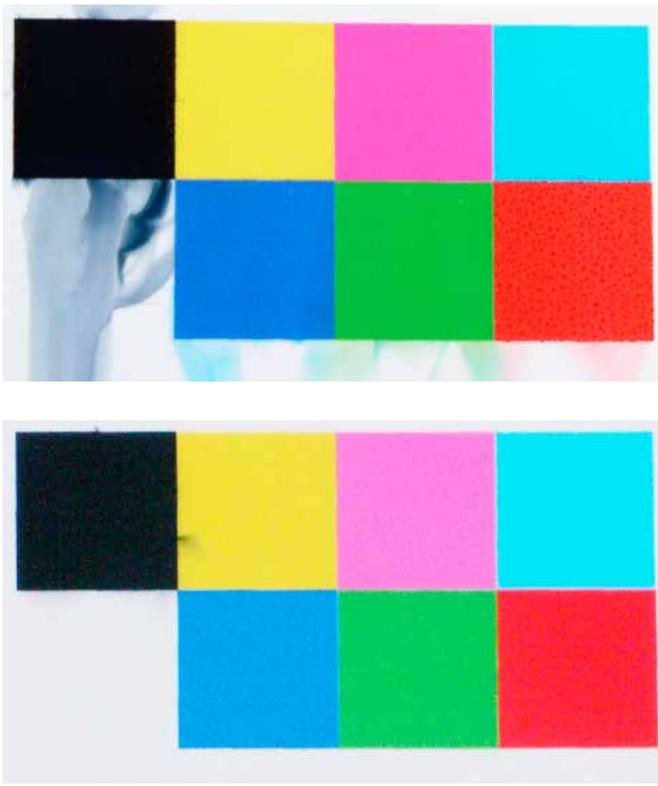


Figure 1.6 Paper coatings without (top) and with crosslinker (bottom) after contacting with water droplets to test the water-fastness

AEROSIL® fumed silica and AEROXIDE® fumed alumina products are characterized by a number of physical-chemical properties that make them very valuable for inkjet media such as:

- A fractal aggregate structure to create microporous coatings with intra- and inter-particle voids and channels
- Small aggregates in the 100–200 nm size range which can be obtained by established dispersing processes yielding coatings with high gloss values.
- An anionic or cationic surface charge

The unique particle structure of AEROSIL® fumed silica and AEROXIDE® fumed alumina products is illustrated in **Figure 2.1**. Due to their structure, they can perform functions in microporous inkjet media that are difficult to achieve with other materials.

2.1 Manufacturing Process

AEROSIL® fumed silica is a synthetic, amorphous silicon dioxide that is produced in an oxygen-hydrogen gas flame through hydrolysis of chloro-silanes according to the following reaction equation:



Evonik Industries developed this technique over 70 years ago and has continuously improved the process. Since it is produced by flame hydrolysis, AEROSIL® is considered a fumed silicon dioxide or fumed silica.

Metal oxides, such as aluminum oxide and titanium dioxide can also be produced using the AEROSIL® process. The reaction equation for aluminum oxide, for example, is as follows:



Evonik markets these fumed metal oxides under the trade name AEROXIDE®. Evonik also produces a number of mixed oxides, providing the most comprehensive product line on the market.

2.2 Purity

Evonik uses very pure raw materials for the production of its fumed metal oxides. That is why AEROSIL® fumed silica has a SiO₂-content of more than 99.8 wt. % (loss on ignition), making it the purest silica on the market. The same applies to AEROXIDE® fumed alumina, which has a purity also exceeding 99.8 wt. %.

2.3 Fine Structure

AEROSIL® fumed silica and AEROXIDE® fumed alumina are white, fine, light powders. These are forming fractal structures which are called aggregates that can be as large as several hundred nanometers. The aggregates, in turn, form loose, micrometer-sized agglomerates that can be easily broken down by dispersing.

2.4 Versatile Product Modifications

In order to meet a wide range of technical demands, multiple AEROSIL® fumed silica and AEROXIDE® fumed alumina grades are commercially available. For example, the specific surface area of AEROSIL® OX 50 amounts to only 50 m²/g, whereas that of AEROSIL® 380 is nearly eight times as high. AEROSIL® 200, our most commonly sold product, has a specific surface area of 200 m²/g.

The surface chemistry and structure of AEROSIL® and AEROXIDE® can also be changed. For instance, it is possible to chemically anchor dimethyl-silyl, trimethyl-silyl or polydimethyl-siloxane groups to the surface of AEROSIL® and AEROXIDE® by chemical reaction with organo-silicon compounds. Products modified like this include AEROSIL® R 972, AEROSIL® R 812 S and AEROXIDE® Alu C 805.

Evonik also offers fumed silica and metal oxide dispersions in water under the trade name AERODISP®.

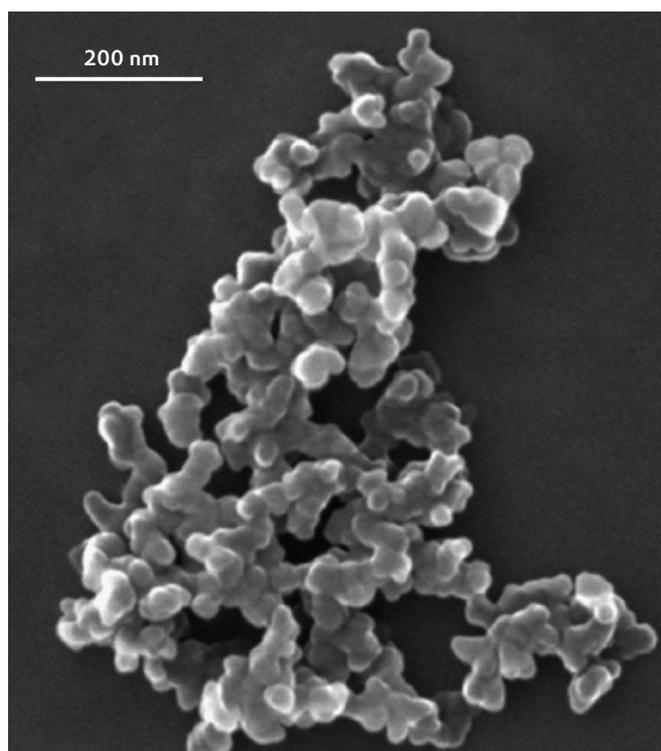


Figure 2.1 AEROSIL® aggregate structure

3 Dispersion

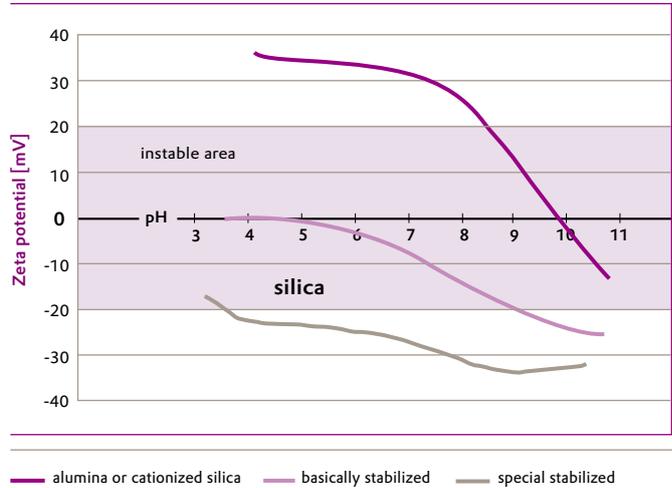
If AEROSIL® fumed silica and/or AEROXIDE® fumed alumina powders are to be used for the production of paper coating formulations, the correct dispersion process is critical. Suitable techniques have been known for a long time and are described in our Technical Information No. 1279. Dissolvers (toothed disk) and rotor/stator systems are successfully used for inkjet dispersions, both in the laboratory and in production.



Figure 3.1 Dissolver (chopper or toothed disk). For best results, the container should have a diameter at least twice that of the disk, yet not be too large. The dispersion shown on the picture was colored for better visibility.

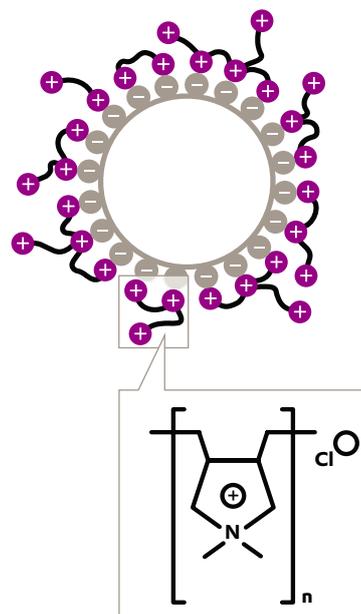
AEROSIL® and AEROXIDE® agglomerates that are present in the powder can be broken down into aggregates having an average size of about 100–200 nm with a relative small energy expenditure. This is the optimum particle size range for glossy inkjet media coatings. The choice of stabilizing agent and pH value (Figure 3.2) to keep the particles from immediately re-agglomerating is as important as the correct dispersion aggregate. Due to the nature of the interaction between ink and media (color brilliance, water fastness), pigments in the inkjet coatings should be positively charged (cationic). For the dispersion of AEROXIDE® fumed alumina, which below approx. pH 10 has a natural positive charge, it is therefore necessary to stabilize the dispersion in the acidic pH range (approx. pH 4). We therefore recommend that an acetic acid/acetate buffer be added during the dispersion of the AEROXIDE® alumina powder.

Figure 3.2 Electrostatic Stabilization. Choosing the proper pH value, makes it possible to prevent re-agglomeration by charging the particles sufficiently so they repel each other. Colloidal systems are unstable within the pink colored region



When dispersing AEROSIL® in the acidic pH region, it is necessary to use a cationic poly-electrolyte that is adsorbed onto the surface reversing their charge from slightly negative to positive. We especially recommend Poly(diallyldimethylammonium Chloride) (p-DADMAC) or cationic silanes e. g. DYNASILAN® DS 1189 with a low molecular weight. There is no need to adjust the pH value of this dispersion. It will automatically be about pH 3 because the cationic polymer “keeps” H⁺ ions away from the silica surface. We recommend the use of approx. 200 to 300 µg of cationic polymer per m² of silica surface.

Figure 3.3 Schematic depiction of a cationized fumed silica particle and chemical formula of p-DADMAC



To prevent flocculation of dispersed fumed silica in the presence of a cationic polymer, add the polymer to water and then disperse the AEROSIL® fumed silica powder. The polymer will then distribute itself on the silica surface. However, care should be taken to use only de-ionized water since ions (e.g., Ca²⁺, Mg²⁺) can reduce the dispersion stability as well as stability of the coating formulation.

Interaction of the particles with one another and stabilizing agents limit the maximum obtainable solids content. As a rule of thumb: the higher the BET specific surface area of the powder, the lower the solids content of the dispersion at a given viscosity. High solids contents at the limits of what is possible may be economically desirable. It should be noted the risk to over-disperse the particles when using high shear energies. The result can be a loss in both, structure and pore volume in the inkjet coating.

Table 3.1 Maximum achievable solids contents of fumed metal oxide dispersions using a rotor/stator dispersion process

Powder	Maximum achievable solids content [%]
AEROXIDE® Alu C	30–40
AEROXIDE® Alu 130	25–30
AEROSIL® 200	20–25
AEROSIL® 300	15–20



Figure 3.4 Rotor-stator mixing head



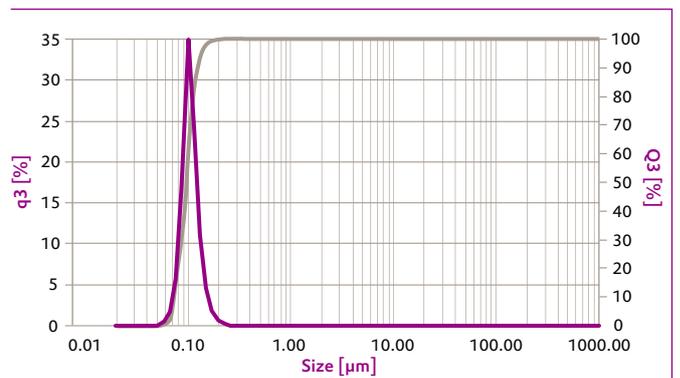
Figure 3.5 Continuous rotor-stator mixer showing the inlet for the AEROSIL® (a) and the liquid (b), and the outlet for the product (c). This system is practically dust-free

A well-balanced dispersion process optimized to the end product plays a major role in the manufacture of inkjet media. An inferior dispersion could result in the following:

- Low gloss
- High viscosity of the coating formulation
- Sedimentation of the pigments
- Low solids content

Over-dispersion, on the other hand, will lead to low pore volumes and reduced ink absorptivity of the coating. Consult us about your dispersion process or use our ready-to-use AERODISP® dispersions that we have customized for this application.

Figure 3.6 Particle size distribution of an AEROSIL® 200 dispersion



4 Ingredients for Microporous Paper Coatings

4.1 Fumed Metal Oxides

Microporous coatings require special pigments which can be chosen from our extensive AEROSIL®, AEROXIDE®, and AERODISP® product line. When selecting a product, pay special attention to the following parameters:

Particle structure

- important in obtaining the highest possible porosity

Particle size

- affects the transparency and gloss

Binder requirement

- changes the porosity of the coating

Cationic surface charge (optional)

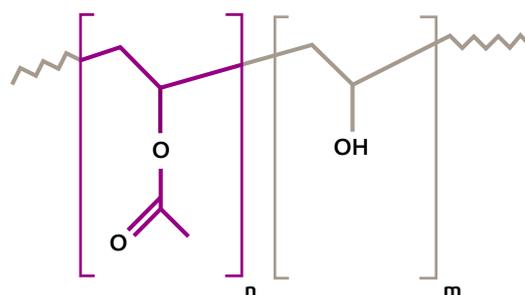
- provides high water-fastness.

Products that best meet these requirements are AEROXIDE® fumed alumina and AEROSIL® fumed silica products with high specific surface areas. Because of their cationic surface charge, AEROXIDE® fumed alumina is particularly suitable for water-fast inkjet coatings. The anionic ink components become bound to the cationic surface when printed and can not be dislodged by water any longer.

4.2 Binders

AEROSIL® products are extremely fine powders and therefore require a binder with the highest adhesive force: polyvinyl alcohol (PVA). The adhesive force of PVA is superior to that of latex and natural binders. Another distinguishing property of PVA is that it forms transparent, colorless films that are compatible with our AEROSIL® products and the paper chemicals generally used.

Figure 4.2 Chemical structure of PVA. Acetate groups (purple) can be split off by hydrolysis to form hydroxyl groups (gray). Besides the molecular weight of PVA, its degree of hydrolysis (saponification) determines its properties



Polyvinyl alcohol is available in a broad range of grades with different qualities. One of the most prominent distinctions between the different grades is the degree of saponification (Figure 4.2), that is the number of acetate-groups (purple, n) which one replaced by hydroxyl-groups (gray, m). The main advantages of partially hydrolyzed PVA are higher flexibility, better adhesion on substrates and better porosity.

Substrate	Use	AERODISP®		AEROXIDE®		AEROSIL®		
		WK 341	WK 7330	Alu C*	Alu 130	200	255	300
Paper	All-Office Paper (see Ref. 9)	■	●					
	Special Inkjet Paper	●	●	●	■			
	High-speed inkjet		●			■	■	■
RC-Photo Paper/Film	Single Layer Coating			■	●	●	●	●
	Base Coating		●	■		●	●	●
	Top Coating	■		●	●	■	■	■

* Products are also available as AERODISP® dispersions (see Ref. 10)
Experimental grades of AEROSIL® and AEROXIDE® are available on request.

● highly recommended ■ recommended

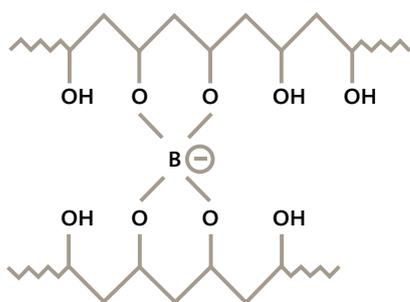
AEROSIL® fumed silica, on the other hand, is anionic. It is therefore difficult to subsequently process dispersions made from silica into cationic coating formulations, because the dispersed silica particles re-agglomerates during the cationization step and precipitates out of the dispersion. The cationic dispersions already described in the previous section provide a solution here, permitting silica to also meet a basic requirement for water-fast printouts.

Another important difference between the different grades of PVA is the median chain length. A longer PVA chain provides higher binder power but also increases the viscosity of the coating formulation. Taking the pros and cons into account, we recommend the grades MOWIOL® 40–88 = PVA 224 or PVA 235, which are produced by Kuraray (Japan). Similar grades are also available under the trade name CELVOL®, which are produced by Celanese.

4.3 Crosslinkers

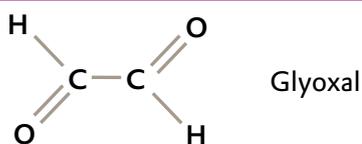
The use of crosslinkers is unavoidable in the application described here because this is the only way to achieve the required open pore coating structure. Since the crosslinker reacts chemically with polyvinyl alcohol, producing coating formulation and drying coated paper pose special challenges. After comprehensive laboratory tests we have identified two types of crosslinkers. Boric acid is particularly suitable for crosslinking neighboring chains of polyvinyl alcohol. This increases the adhesive force of PVA, thereby permitting a smaller binder amount. This, in turn, results in a more porous coating structure with higher absorptivity capacity.

Figure 4.3 Boric acid-crosslinked adjacent polyvinyl alcohol chains



Since it is not possible to obtain outstanding water-fastness with boric acid alone, it is advantageous to use a second crosslinker. Compounds based on dialdehydes, such as glyoxal, have proven themselves for this application. In particular, the product CARTABOND® TSI (Clariant) has demonstrated very good performance.

Figure 4.4 Chemical formula of Glyoxal



In contrast to molecular glyoxal, it consists of a glyoxal-resin and does not cause yellowing if the coating is exposed to light. It does not increase the adhesive force as much as boric acid, but greatly improves water-fastness of the coating.

4.4 Other Additives

Generally, a formulation for microporous coatings should consist of as few additives as necessary to maintain the porous network structure provided by the particles. Every additional additive requires some space within the network and therefore lowers ink absorptivity. Additives can also have a big impact on binder demand and gloss. Nevertheless, some additives may be inevitable for process reasons and can be categorized as follows.

Cationic polymers or cationic silanes can help to improve compatibility between anionic and cationic components of the formulation, especially if the mixing equipment used is not efficient enough. Therefore, poly-DADMAC or DYNASILAN® DS 1189 (see Chapter 3) may be added to the anionic binder before mixing it with the cationic fumed metal oxide dispersion.

Surfactants (wetting agents) may be necessary for certain coating processes. For example, curtain coating (Figure 6.5) requires a very low surface tension of the formulation to ensure a stable curtain.

Additives for rheology control can help to increase solids content of the formulation or simply to tailor the behavior of the flow curve required by the coating process. Alcohols or glycols have been proven to lower the viscosity of the formulation, but require special attention during the drying process.

Defoamer might be used as well because foam or single air bubbles are potential reasons for coating defects. Nevertheless, and this applies for all additives in this section, if mechanical means can be used rather than chemical additives they are strongly preferred. Defoaming and/or degassing of coating formulations, for example, can easily be achieved by using vacuum type dissolvers or other mechanical degassing units.

5 Paper Coating Formulations and their Make-up

The paper coating formulations discussed in this technical information are based on our own experiences in the laboratory and on pilot coating machines. They should give end users a successful start in their own development projects involving AEROSIL®, AEROXIDE® and AERODISP® products. Before we go into further detail, however, let us first make some suggestions regarding the use of dispersions when preparing coating formulations. Due to their positive surface charge, dispersed cationic particles readily react with anionic coating components resulting in flocculation and precipitation of agglomerated anionic and cationic particles. To prevent this, it is necessary to process the coating formulation components in such a sequence that the surface charge differences, when a new component is added, are as small as possible.

Our customary batch sequence is as follows:

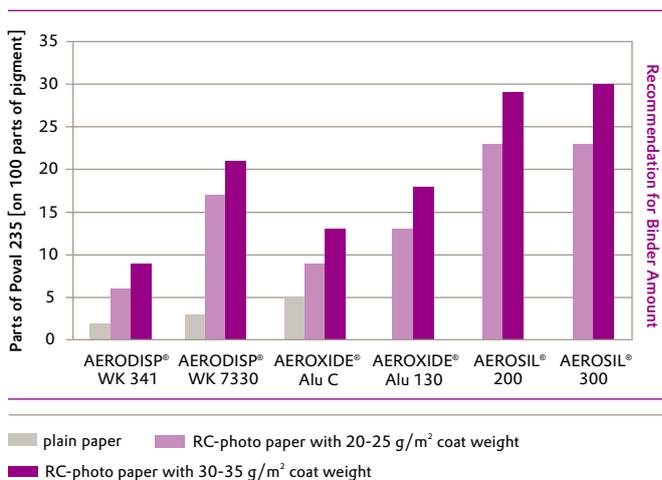
- 1 Combine the PVA-solution and cationizing agent and dilute with water to the desired concentration
- 2 Prepare the AEROSIL® or AEROXIDE® dispersion according to chapter 3 or add an AERODISP® dispersion
- 3 Add crosslinkers

As an option it is possible to change the sequence of addition by initially filling the batch tank with a (larger) quantity of AEROSIL® or AEROXIDE® dispersion in order to take machine restrictions into account and provide a higher starting liquid level for the agitator.

- 1 Prepare the AEROSIL® or AEROXIDE® dispersion according to Chapter 3 or add an AERODISP® dispersion
- 2 Add the PVA-solution including cationizing agent (cationized PVA) after adjusting the desired water content
- 3 Add crosslinkers

Before you begin machine trials, we recommend that the corresponding formulations first be tested in the laboratory or pilot scale to avoid unanticipated problems. When adding boric acid, please note that the coating formulation will obtain a much higher elastic viscosity which will drop again when the temperature is increased. Therefore it is recommended to add the boric acid slowly.

Figure 5.1 Binder demand of various AEROSIL®, AEROXIDE® and AERODISP® products in a cross-linked coating formulation with 12.5% boric acid and 2% CARTABOND® TSI (relative to the PVA) on plain paper (grey), RC-photo paper with 20–25 g/m² coat weight (light purple), and RC-photo paper with 30–35 g/m² coat weight (dark purple).



Recommendation for Binder Amount

■ plain paper ■ RC-photo paper with 20-25 g/m² coat weight
 ■ RC-photo paper with 30-35 g/m² coat weight

6 Coating and Drying Technologies

We perform extensive coating tests in the laboratory and on pilot-machine scale to test our products and develop coating formulations as guidelines for our customers.



Figure 6.1 Manual paper coating in the laboratory

The results which will be presented and discussed in **Chapter 7** of this technical information are the product of comprehensive laboratory work followed by multiple test runs



Figure 6.2 Paper coating with a casting knife

In the laboratory, we use conventional profiled hand bars with wet-film thicknesses between 24–150 μm . PET films, RC papers and coated base papers serve as substrates. The papers are dried with a hot blast or with a conveyor drier that operates on the basis of convection and IR. This approach permits the development of guide formulations and establishes basic product performance data. In addition, tests with a suitable pilot machine are necessary.

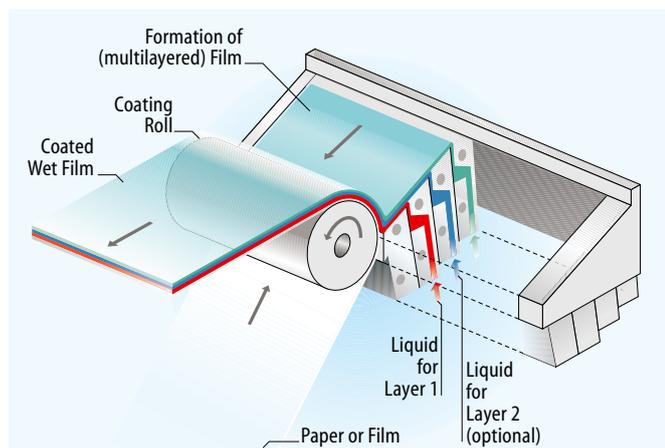
on a pilot coater. The pilot coating machine shown in **Figure 6.3** has a casting knife with a variable gap and coating width of approx. 31 cm. It especially enables the application of wet films with a thickness of 60–210 μm at a typical web speed of approx. 5 meters per minute. The coating machine also has a 6 meter long float drier which allows the independent drying of top and bottom side of the paper by means of a temperature profile divided into three sections.



Figure 6.3 Pilot production coater (UBW Universalbeschichtung Wolfen GmbH, Germany)

6.1 Slide Coating

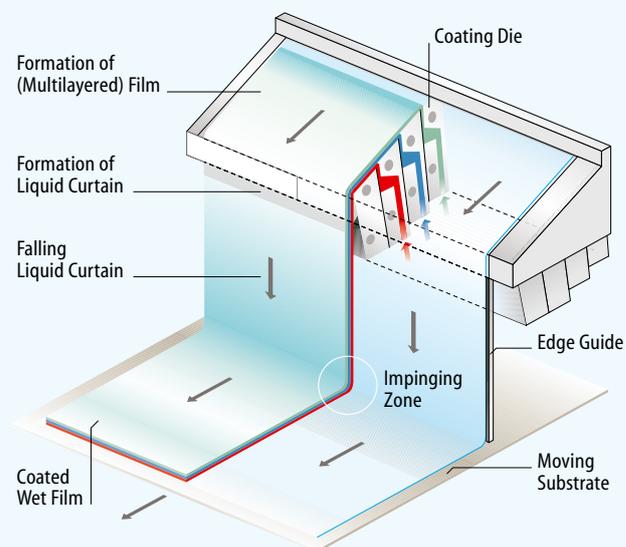
Figure 6.4 Slide Coater



Slide coating is a widely used coating method from the field of silver-salt photography. It permits the simultaneous application of several coating layers. The coating formulations need to exhibit laminar flow to prevent turbulence that would otherwise occur between layers due to the inclined run. This means that particularly high requirements must be taken into consideration when coating formulations are developed.

6.2 Curtain Coating

Figure 6.5 Curtain Coater



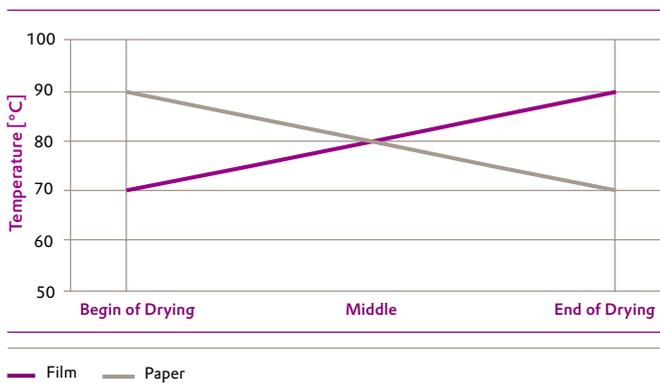
A further development of slide coating is curtain coating. In this non-contact process, free-flowing coating formulations are poured onto the substrate. A slice (nozzle), which has the same width as the web, is used to produce the curtain. The strictly specified slice and uniform flow from the slice produce a homogenous high-quality coating with constant coat weight. The coating formulation, however, must not contain any enclosed air and needs a certain elasticity in order to ensure stability of the curtain. Elasticity is also required, since the coating is stretched when it comes into contact with the fast-moving substrate. Please see ref. 8 for more details.

7 Performance of Microporous Inkjet Paper Coatings

6.3 Drying

Drying glossy coatings on non-porous substrates, such as RC paper, is a technical challenge. Unlike paper coatings without an RC barrier layer, the evaporation of water can take place only on the coated side. Correct adjustment of the drier is therefore very important. Since quantities of water to be evaporated are large, industrial applications require driers that are from 30 to 100 meters long. The length of the drier is subdivided into several drying zones. Various temperature profiles which affect the quality of the coating, can be obtained through the temperature settings of the drying zones. Our tests have shown that it is advantageous for the air temperature to rise during the drying process of coated non-porous substrates. This careful procedure starts at temperatures of 70–80°C and ends at temperatures of approx. 90 to slightly over 100°C.

Figure 6.6 Recommended temperature profiles for the drying of coated non-porous substrates like film or RC-paper versus coated plain paper



7.1 Absorption

The absorption capacity of a microporous inkjet coating is difficult to quantify. Therefore, images will be used in this chapter to demonstrate the qualitative differences in ink absorption. **Figures 7.1** and **7.2** depict samples in which the absorption declines.

The undesired pattern that arises is called mottling. Mottling is caused by individual inkjet droplets that run together due to a lack of absorption capacity on the coating surface. The binder requirement should therefore always be optimized to the minimum amount of binder needed (**Figure 7.1**). Also the thickness of the coating largely determines its ink adsorbivity (**Figure 7.2**). A higher coat weight naturally raises the pore volume as a whole.

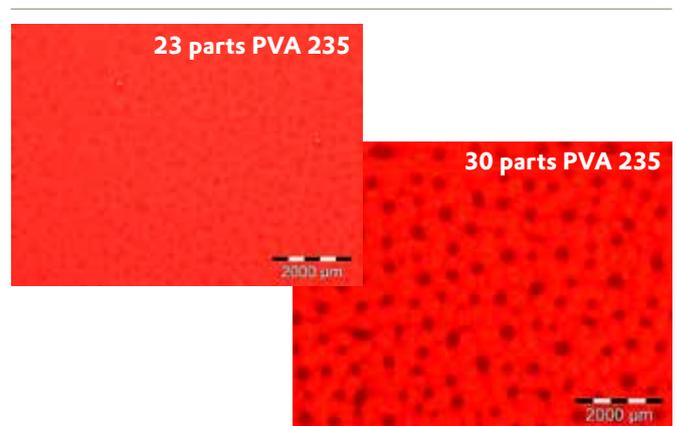


Figure 7.1 Influence of the binder amount of an AEROSIL® 300 based coating on image quality. The higher binder content (lower picture) leads to distinct mottling.

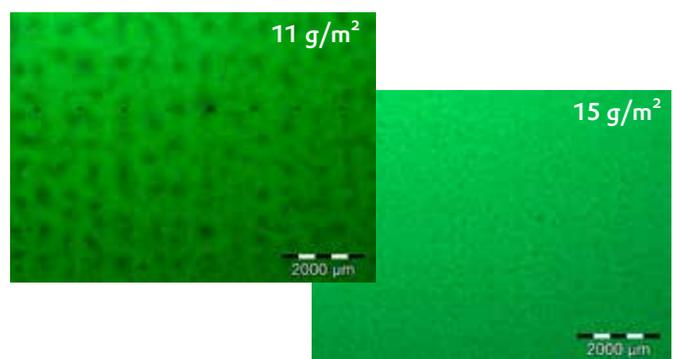


Figure 7.2 Influence of coat weight of an AEROSIL® 200 based coating on image quality. The lower coat weight (left) results in pronounced mottling.

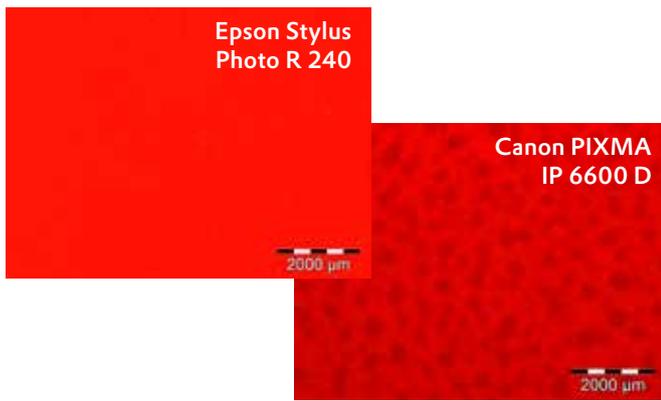


Figure 7.3 Different printers require different media (AEROSIL® 300 based coating)

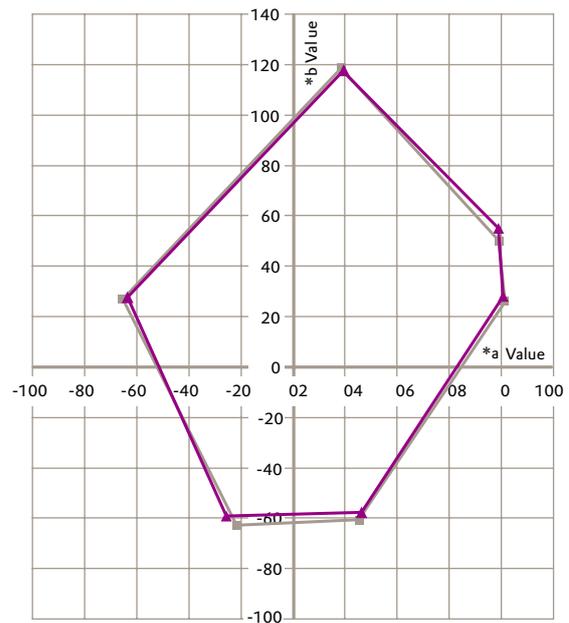
Different kinds of particles also influence the absorption capacity of a coating. This could already be seen in **Figure 1.3** in **Chapter 1** where different fumed alumina grades were compared in terms of the resulting pore size distributions. In general, fumed particles show very high specific pore volumes compared to precipitated metal oxides. As a rule of thumb, higher BET materials lead to higher pore volumes. Also important is the specific density of a pigment. This is why AEROXIDE® Alu 130, a fumed alumina with a specific surface of 130 m²/g has a similar pore volume as AEROSIL® 200 with a specific surface area of 200 m²/g. Fumed metal oxides with low specific surface areas like our alumina-doped fumed silica in AERODISP® WK 341, are especially recommended for substrates which already exhibit sufficient absorptivity of their own, such as plain paper.

The image quality of a specific coating also depends on the printer and particularly on the ink used. For example, the absorption capacity of an AEROSIL® 300-based coating shown in **Figure 7.3** is adequate for a printer like the Epson Stylus Photo R 240 (picture at the top). Other printers, however, dramatically place other requirements on the coating. This is true for older printers, as well as modern printers, like the Canon PIXMA iP 6600 D (bottom picture in **Figure 7.3**), which can produce mottling on the same coating. A coating with a larger coat weight would be needed in this case to guarantee perfect image reproduction. The latter mentioned printers use dye-based inks that generally need coatings with higher absorption capacities than pigment-based inks.

7.2 Color Brilliance

Coatings based on fumed alumina, such as AEROXIDE® Alu C and AEROXIDE® Alu 130, truly distinguish themselves through their high color brilliance or large gamut (**Figure 7.4**). The gamut obtainable with AEROSIL® fumed silica is generally somewhat lower but can be improved by adding approximately 10% AEROXIDE® fumed alumina.

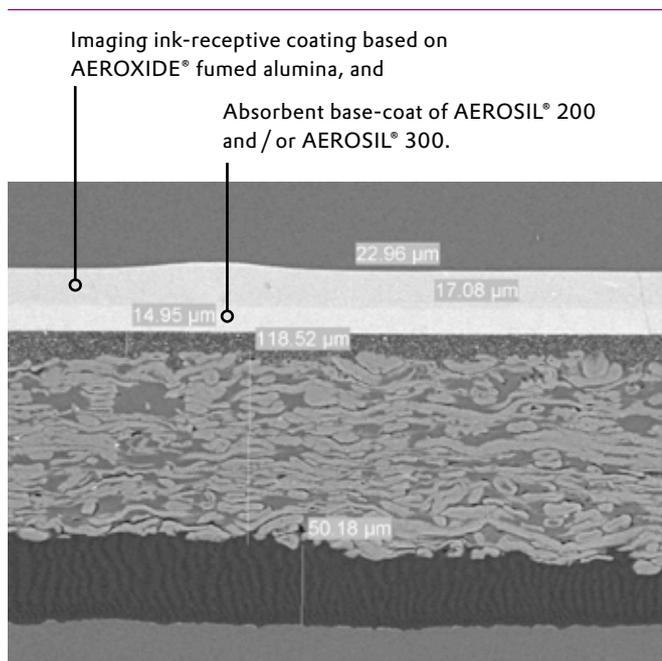
Figure 7.4 a*b* diagram measured on six color fields: yellow, magenta, cyan, red, blue and green. The area inside the plotted lines is a measure of the color brilliance



This also increases the effective absorption capacity of the coating. In general, our products are compatible with one another so that synergetic effects can be obtained by mixing them.

Another cost-effective method to optimize gloss is the application of a double coating (Figure 7.5). This consists of an imaging ink-receptive coating, based on AEROXIDE® fumed alumina, and an absorbent base-coat of AEROSIL® 200 and/or AEROSIL® 300.

Figure 7.5 SEM image of the vertical section through an inkjet photo with two microporous layers on topside



7.3 Gloss

The extreme fineness of AEROSIL® and AEROXIDE® particles enables the manufacture of microporous photo inkjet papers with high gloss. Our pilot coating runs yielded the following typical gloss values for paper coatings measured at an angle of 60° (Table 7.1 and also Figure 7.6). These gloss values were measured on samples with 20–35 g/m² coat weights. Higher values can be obtained depending on the quality of the coating.

Table 7.1 Gloss values of paper coatings manufactured with AEROSIL®, AEROXIDE® and AERODISP® products

Powder	Typical gloss values
AERODISP® WK 341	39 – 42
AERODISP® WK 7330	27 – 31
AEROXIDE® Alu C	33 – 37
AEROXIDE® Alu 130	40 – 46
AEROSIL® 200	34 – 39
AEROSIL® 200	34 – 39
AEROSIL® 300	34 – 39



Figure 7.6 Visual assessment of gloss and other image properties

8 Frequently Asked Questions

Many unexpected difficulties are encountered on the path from the facts presented in this technical information to the successful development of a new product. The scale-up from the laboratory to commercial production is particularly challenging. Below, we have attempted to compile answers to the most common problems encountered by customers in the past, or that we ourselves have experienced and eventually solved. If your question is not included, do not hesitate to ask us directly!

Question 1:

The microporous coating has surface defects in the form of cracks! What happened? How can I prevent this?

Microporous coatings should be prepared with a minimum amount of binder to attain maximum porosity and absorption capacity. The low binder content results in higher stress within the layer during drying and this can cause cracks.

Figure 8.1 shows what happens when the binder amount is too low.

These cracks are generally called “microcracks.” They appear when individual parameters, like coating thickness, solids content of the coating formulation, binder amount used, binder type, pigment type, additives, drying conditions, and so forth, do not match one another.



Figure 8.1 Microcracking

But the single most important reason for microcracks is a too little binder content in the coating formulation. Microcracking can then be effectively prevented by increasing the amount of binder by 10 to 30% while keeping the other parameters the same.

Question 2:

The microcracks disappeared after binder amount was increased, but cracks reappeared after printing. What should I do?

Microcracking appears in a variety of forms. The “print cracking” described here first becomes visible (**Figure 8.2**) when binder amount drops just slightly below the minimum amount needed. In this case, it is enough to increase binder amount by approx. 5–10% to prevent cracking. If major cracking occurs, like that shown in **Figure 8.1**, the binder amount needs to be increased by approx. 10–30%.

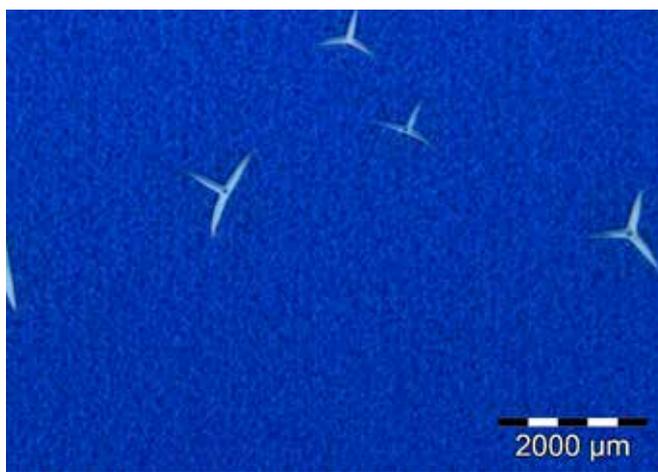


Figure 8.2 Print cracking

Question 3:

Adding a supplementary agent resulted in extremely strong cracking of the surface or the gloss was lost!
How can I eliminate the problem?

The cracking shown in Figure 8.3 is caused by a breakdown in the coating structure. The supplementary agent is likely incompatible with the microporous coating or changes surface tension of the coating formulation too much. We recommend testing a different supplementary agent or trying to work without one.



Figure 8.3 Extreme Cracking

Question 5:

How is “binder demand” defined?

When a formulation is specified in Europe, binder demand of a coating formulation is usually calculated as the amount of binder used relative to the (solid) amount of pigments. In other regions, however, binder demand is usually quoted as the ratio between pigment and binder. Table 8.1 is a simple conversion table to clarify the binder information in various regions.

Table 8.1 Comparison of different conventional units specifying the binder demand

Binder demand	Pigment-to-binder ratio	Binder amount
Parts dry binder to 100 parts pigment		Percentage of binder in the final coating (without volatile components)
6	16.67	5.7
8	12.5	7.4
10	10	9.1
12.5	8	11.1
16.67	6	14.3
25	4	20.0
50	2	33.3

Question 4:

What parameters affect cracking?

Other parameters that cause or affect cracking are as follows:

Coating thickness, coat weight	Larger coating thicknesses or higher coat weights require more binder.
Solids content of the coating formulation	Coating formulations with higher water content require more binder.
Drying	Too strong drying or wrong profile causes extensive cracking.
Binder grade	Short-chained PVA has less adhesive force than long-chained PVA.
Crosslinker	The use of crosslinkers can very effectively reduce the necessary binder amount.
Pigment type	Fumed silica grades with high specific surface areas above 200 m ² /g require much more binder than fumed alumina products with specific surface areas between 100 and 130 g/m ² .
Additives	Small quantities of inappropriate defoamers, wetting agents, etc. can drastically increase the binder requirement.
Defects on the substrate	The substrate should be of high quality. It must also be free of dust before and during the coating.
Coarse particles in the dispersion and/or coating formulation	This can result in isolated cracks. Better dispersion and sifting/filtering – possibly also sedimentation – can help here.

Question 6 :

What happens when there is too much binder?

Excess binder amount that is no longer needed to bind the coating pigments together will penetrate into the porous network. It will fill the pores and thereby reduce the absorptive capacity of the coating. **Figure 8.4** shows the difference between a coating with the optimum binder amount versus a sample with a too high binder amount. The latter coating (bottom picture of **Figure 8.4**) shows distinct mottling as a result of its lower ink absorptivity. Ink droplets collect into large visible drops on or near the surface of the coating (see also **Chapter 7.1**).

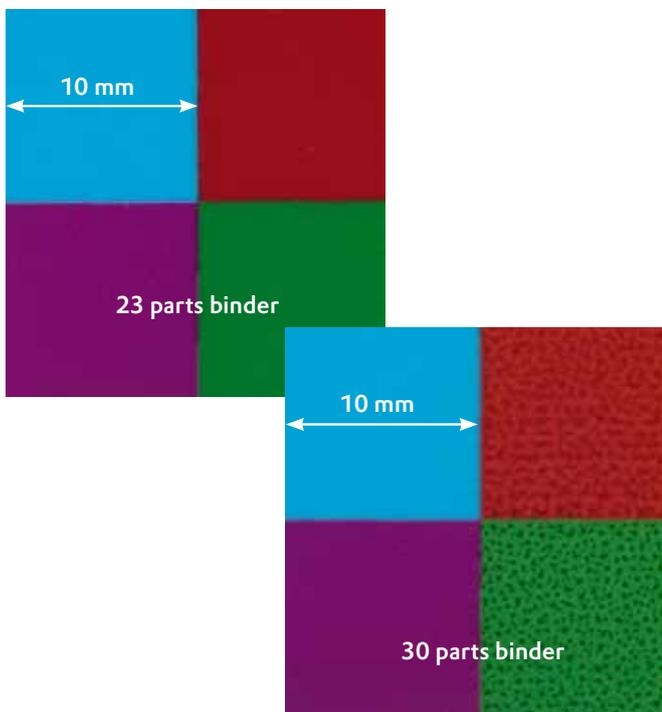


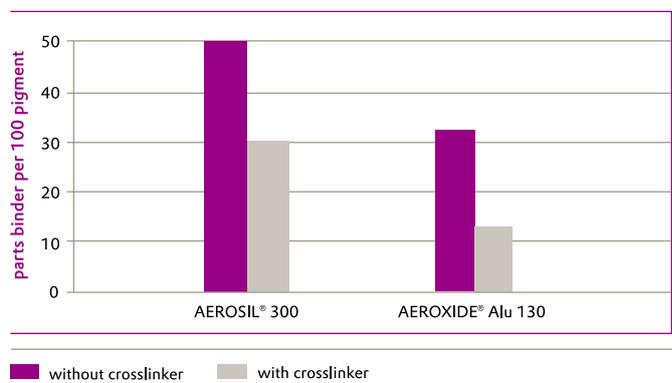
Figure 8.4 Influence of the binder amount on image quality. The higher binder content (lower picture) leads to distinct mottling

Question 7:

How large of an influence does a crosslinker have on the binder requirement?

The use of boric acid as a crosslinker can significantly reduce the required binder amount. **Figure 8.5** shows binder demand of AEROSIL® 300 as well as AEROXIDE® Alu 130 based coatings with PVA 235 as the binder. Crosslinking with boric acid (red columns in **Figure 8.5**) allows a significant reduction of the binder demand in both formulations versus those without crosslinker (blue column). Please see also **Chapter 4.3** for additional information.

Figure 8.5 Binder demand with / without crosslinker



Question 8:

What happens when a crosslinker is used in a coating formulation?

Basically, a chemical reaction takes place between the crosslinker and other components within a formulation, resulting in the formation of stable chemical bonds. This has a direct effect on the physical properties of a coating formulation and after the coating is dried. The viscosity of the coating formulation containing crosslinker thus rises, increasing the visco-elastic properties. If temperature of the formulation is increased, for example, to 50 °C, the viscosity again drops significantly and the coating formulation can be easily processed. Ideally, crosslinking will take place at appropriately high temperatures during the drying process. Let there be no mistake, however, that crosslinking can occur earlier and that crosslinking is also not necessarily complete after the drying. Here too, it is important to optimize the process.

Question 9:

My coating displays circular defects that already appear before the drying?

So-called fish eyes result when surface tensions of the substrate and coating formulation do not match. As a general rule, surface tension of the coating formulation should be lower than that of the substrate in order to prevent wetting defects such as fish eyes. The use of "corona" or plasma systems to increase surface tension of the substrate has proven effective in practice. Also a primer can be applied to the substrate to increase its surface tension.

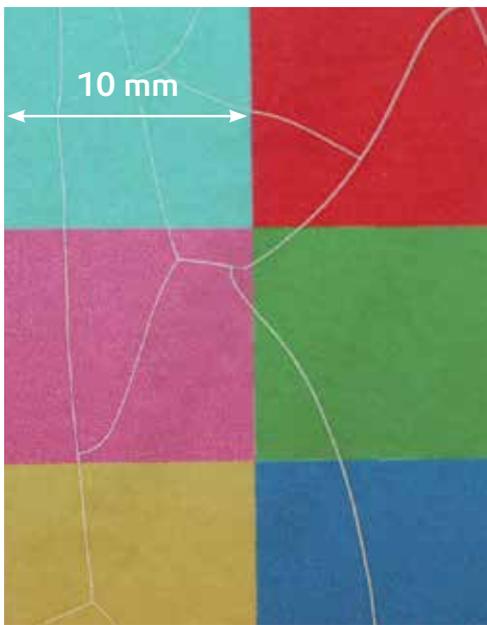


Figure 8.6 Drying cracks

Question 10:

What causes drying cracks?

Drying cracks as shown in Figure 8.6 are the result of too rigorous drying conditions. When drier temperature is too high or a wrong temperature profile is used, a lateral stress will arise within the coating causing cracks. Lowering the drying temperature in combination with a reduction of web speed will very likely resolve the problem.

Question 11:

I would like to increase the transparency of my coating. How do I do this?

Transparency of a coating is determined by its light scattering properties. Three parameters are important.

- 1 The difference between the refractive index n_D of the particles (SiO_2 : 1.46, Al_2O_3 : 1.69) and the pores (mainly air: 1.0). The smaller the difference, the more transparent the layer. Filling the pores with a liquid or a polymer that has an appropriately high refractive index, for example, after printing, can lead to completely transparent coatings.
- 2 Size of the primary particles as well as the aggregates of the pigment(s) used. This means that AEROSIL® 300 based coatings are generally more transparent than AEROSIL® 200 coatings. Better dispersion resulting in smaller aggregates leads to higher transparency.
- 3 The thickness of the coating itself. Thinner coatings are usually more transparent.



Figure 8.7 Appearance of undesired print gloss

Question 12:

Why do some coatings have differences in gloss between printed and unprinted areas?

In **Figure 8.7**, the sample on the right has a lower ink adsorbivity than the one on the left, directly resulting in print gloss because the inkjet ink concentrates itself on the surface and contributes to the gloss. In an extreme case this leads to a kind of negative pattern in the image.

Question 13:

After adding a supplementary agent, I lose the gloss on my coating completely. It now appears semi-matt!

The supplementary agent is likely incompatible with the cationic coating. We have, for example, observed that anionic supplementary agents can cause micro-flocculation reducing or completely eliminating the gloss. The only solution is to test the compatibility of any new supplementary agent with the coating beforehand.

Question 14:

The coating is not completely water-fast, even though I already added boric acid! What can we do?

To further improve water-fastness of a coating containing boric acid, we recommend adding CARTABOND® TSI (Clariant). It does not result in as rigid a crosslinking as boric acid, but drastically reduces the solubility of the binder. CARTABOND® TSI is a glyoxal-based resin and, in contrast to molecular glyoxal, does not cause any yellowing of the coating. We recommend a quantity equal to about 2% of the polyvinyl amount that is used. Please see also **Chapter 4.3** for additional information.

9 The Most Suitable Products for Photo Inkjet Media at a Glance

AEROXIDE® fumed alumina products

	AEROXIDE® Alu 65	AEROXIDE® Alu C	AEROXIDE® Alu 130
BET specific surface area	65 m ² /g	100 m ² /g	130 m ² /g
X-ray form (approx.)	θ and δ, little γ	33 % δ, 66 % γ	γ
Spec. gravity	approx. 3.2 g/cm ³ (depending on ignition loss)		
pH (4% aqueous slurry)	4.5 – 6.0	4.5 – 5.5	4.4 – 5.4
Loss on ignition at 1000 °C	< 3.0 wt. %		
Refractive index, n _D	1.69		

AEROSIL® fumed silica products

	AEROSIL® 200	AEROSIL® 255	AEROSIL® 300
BET surface area	200 m ² /g	255 m ² /g	300 m ² /g
Spec. gravity	approx. 2.2 g/cm ³ (depending on ignition loss)		
pH (4% aqueous slurry)	3.7 – 4.5	3.7 – 4.5	3.7 – 4.5
Loss on ignition at 1000 °C	≤ 1.5 wt. %	≤ 1.5 wt. %	≤ 2.0 wt. %
Refractive index, n _D	1.46		

Aqueous dispersions based on AEROSIL® fumed silica and AEROXIDE® fumed alumina

	AERODISP® WK 7330	AERODISP® WK 341	AERODISP® W 630	AERODISP® W 440
Base material	Silica, cationized	Silica, cationized	Alu C	Alu 65
Solids content	30 wt. %	41 wt. %	30 wt. %	40 wt. %
pH-value	2.5 – 4.0	2.5 – 4.0	3.0 – 5.0	3.0 – 5.0
Appearance	White, milky and low viscous liquids			
Median aggregate size	~ 120 nm	~ 140 nm	~ 140 nm	~ 120 nm
Surface charge	+ Cationic (positively charged)			

The data represent typical values and not production parameters. Developmental products are labeled with the VP designation. Their commercialization depends on market response. Even though they are produced in commercial quantities, future availability should be verified.

10 Experimental Details

The general statements made in this paper are based on extensive laboratory and pilot plant studies. Beside of our own materials, we used MOWIOL® 40–88 and POVAL 235 (both from Kuraray, Japan) as the main binders, POLYQUAT 40 (Katpol, Germany) as cationic polymer, and boric acid as well as CARTABOND® TSI (Clariant, Switzerland) as crosslinkers.

For each formulation the optimum binder amount was determined by preparing and analyzing coating formulations with increasing binder quantities. RC coated photo base paper with a grammage of 220 g/m² was used as substrate. Coat weights were determined by weighing parts of the coated paper cut by a circle cutter.

After storing under standard climate conditions (23 °C, 50% rel. humidity) for at least 24 h, the coated papers were printed on four different printers (Epson Stylus Color 980, Epson Photo Stylus R 240, HP Deskjet 5652, Canon iP 6600 D) using the print pattern in **Figure 7.6**. This print pattern which was created with CorelDRAW® software contains the various elements needed for quantifying print attributes such as optical density, color gamut area, mottling etc. Images were analyzed visually using clearly defined evaluation criteria as well as automatically with a spectrophotometer (SpectroEye, GretagMcBeth). Gloss measurements were carried out at 20°, 60°, and 85° Bragg angle using the method of Lehmann (Micro-Tri-Gloss, Byk).

11 References, Additional Literature

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