# Tailor-Made Silica and Alumina for Inkjet Media Coatings

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## Abstract

The optical properties and printability of modern, microporous inkjet media is strongly controlled by the type of the pigments used inside the coating. It is well known that coatings based only on commodity pigments like clay or calcium carbonate cannot meet today's requirements. The use of amorphous, synthetic silica or alumina is not only setting the limits of conventional coatings, but is also making functional high performance pigments the key to meeting current and future requirements. These modern materials provide special pore structures and surfaces for the adsorption of dyes and/or color pigments resulting in properties like excellent image density, outstanding resolution and instant drying.

This paper gives an overview over the physical-chemical properties of special synthetic pigments and their relation to the parameters of the coating process and the resulting optical properties of the media. Such aspects as the pigment composition (silica, alumina, mixed oxides), the pigment formation process (fumed, precipitated), the particle size and structure, the dispersion process and the formation of the coating formulation are correlated with media properties like gloss, ink adsorption, and image quality.

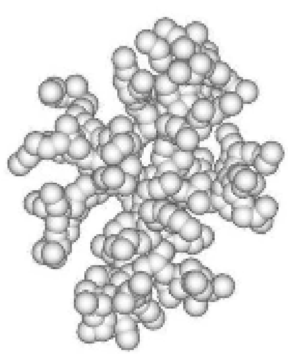


*Figure 1. Model of a fumed oxide particle (aggregate).*

## Introduction

Today, synthetic silicas and aluminas are the principle constituent of microporous inkjet media coatings and are basically responsible for their performance. Fumed materials, that is, materials produced within a flame, whose particle sizes lie far below 1 μm are used for glossy coatings to a great extent, whereas matte coatings rely on synthetic silicas from precipitation processes. Their particle sizes amount to several μm. Both types of materials share the common trait that the particles have specific surfaces ranging from 50 to 700 $m^2/g$. In the printed image, this surface serves as a carrier of dyes and/or dye pigments. At the same time, the particles possess pores (precipitation products) or form voids and capillaries in the layer due to their unique fractal structure. These voids and capillaries make it possible to absorb the water of the ink droplets within fractions of a second, thereby giving the media its characteristic instant-dry behavior.

### Production and Properties of Fumed Oxides

Fumed oxides are produced from volatile precursors in a detonating gas flame in a gas-phase process. The production of fumed silicas,[1] which Degussa markets under the trade name AEROSIL®, proceeds according to the following chemical equation:

$$SiCl_4 + 2\,H_2 + O_2 \rightarrow SiO_2 + 4\,HCl \quad (1)$$

Alumina, titania, and other oxides can also be produced according to the same principle,[2] provided that vaporizable educts exist. Besides this process for producing pure oxides, there still exist other variants for producing mixed oxides or doped oxides for which the entire periodic system of the elements is open in principle.

It is common to all fumed oxides that spherical primary particles of a few nanometers in diameter, which later on form tightly intergrown aggregates[3] with fractal structure, are first generated within the flame (see Figure 1). These aggregates can no longer be milled into primary particles through any processes known today.

Together with other aggregates, especially when in powder form, these aggregates form rather loosely bound agglomerates,[3] whose overall sizes lie in the μm range.

At this point, it is necessary to emphasize that, in contrast to the precipitated particles, the particles are not porous themselves, but that interparticular voids and capillaries, which distinguish the microporous coatings, are formed only by packing the particles into a layer.

**Custom Dispersions for Glossy Inkjet Media**

The first step in producing a coating formulation is to disperse the particles in water. This breaks the agglomerates, and even the larger aggregates and distributes them within the dispersion medium. The important thing in this step is that the particles are stabilized immediately, preventing their reaggregation. In aqueous media, electrostatic stabilization of the particles themselves is usually used. In other words, the pH value is utilized to adjust the surface charge (zeta potential) of the particles in such a manner that the particles mutually repel each other (see Figure 2).

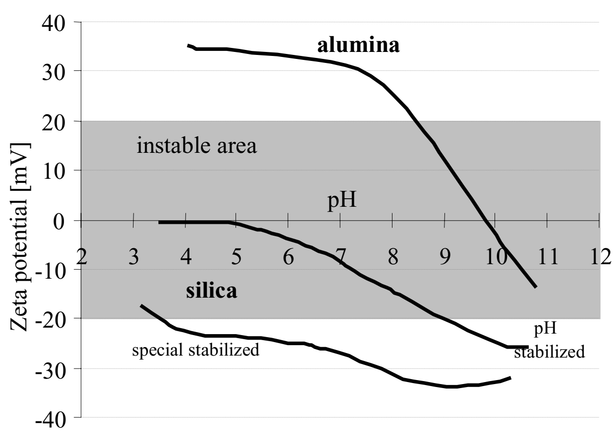



*Figure 2. Zeta potential curves of different alumina and silica dispersions*

To optimize the adsorption of the mostly anionically charged ink dyes on the particle surface and thus achieve the known water fastness of the microporous inkjet media, the particles should be oppositely charged at least in the topcoat, which is to say cationic. This is of course true for alumina. For silicas, a surface modification with special cationic polymers is employed, resulting in a zeta potential curve nearly identical to the curve for alumina.

The interaction of particle size, viscosity, solids content, and binder demand is essential for the successful introduction of a pigment dispersion into a coating formulation. These parameters can be controlled within limits by selecting and controlling the right dispersion process. Here it is necessary to find the optimum economic efficiency and performance for each system.

**Production and Properties of Precipitated Silicas for Matte Media**

Whereas fumed oxides are synthesized in the gas phase, wet-processed silica arise in the aqueous phase. The raw materials are waterglass and sulfuric acid:

$$Na_2SiO_3 + H_2SO_4 \rightarrow (H_2SiO_3) + Na_2SO_4 \rightarrow SiO_2 + H_2O + Na_2SO_4 \quad (2)$$

The silicic acid that is generated by acidifying waterglass is unstable and decomposes into insoluble silica and water. The $SiO_2$ produced in this manner is amorphous and consequently very porous. It forms aggregates with firmly coalesced primary particles in the size range of a several μm (see Figure 3). This gives rise to a very large internal surface of as much as 700 $m^2/g$ and a pore structure as found in a sponge. The pore diameter ranges from a few nanometers to more than 50 nm. In contrast to the fumed oxides described above, the primary particles, which come into existence only during precipitation, adhere more tightly to each other so that the aggregates arising from them are more difficult to separate from each other. The pore structure is retained even when the silica is subjected to mechanical handling, such as milling. The particle size of the aggregates determines the matting effect. The pore structure of the particles determines the other properties of the inkjet media that are important for the image. The trade name of these products is SIPERNAT®.

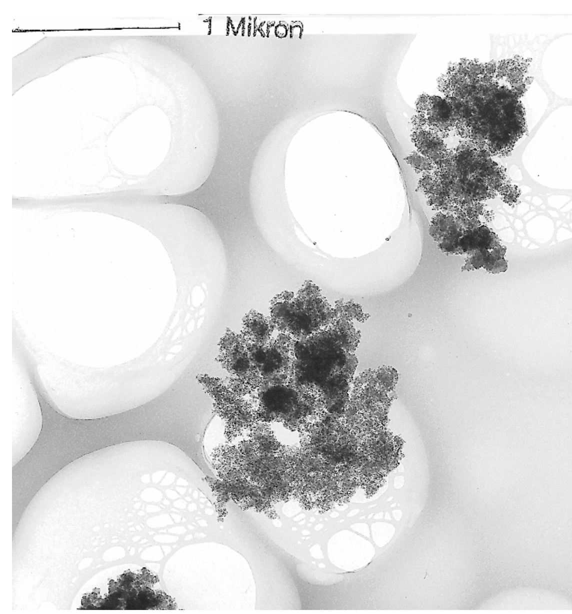



*Figure 3. TEM of SIPERNAT® 570 showing its unique sponge structure, the key for highest absorptivity and lowest ink drying time of matte ink jet coatings*

## Experimental

### Materials

**Table 1. Dispersions for Glossy Inkjet Media**

| | AERODISP® . WK 341 | Experimental Dispersion, BET ~130 m²/g | AERODISP® W 630 |
|---|---|---|---|
| Base material | doped silica | silica/ doped silica | alumina |
| Solids content | 41% | 30% | 30% |
| pH | 2.5-4 | 2.5-4 | 3-5 |
| appearance | milky white liquid, low viscous | | |
| av. aggregate-size (median) | ~140 nm | ~120 nm | ~130 nm |
| surface charge | Cationized | | cationic |

**Table 2. Materials for Matte Inkjet Media**

| | BET [m²/g] | DBP [g/100g] | Particle size; $d_{50}$ [µm] |
|---|---|---|---|
| SIPERNAT® 310 | 750 | 210 | 5.5 |
| SIPERNAT® 350 | 50 | 210 | 3 |
| SIPERNAT® 570 | 750 | 250 | 6.7 |
| EXP 5400-2 | 375 | 240 | 6.6 |
| EXP 9012-2 | 175 | 225 | 11 |

### Dispersing and Dispersion Measurements

Unless stated otherwise, standard Degussa products were used as dispersions. The dispersions were characterized in the standard manner in terms of viscosity, particle size, pH, and solids content. The Horiba LA-910 particle size analyzer was used to measure the particle size (static light scattering, measurement range 20 nm to 1000 µm). Particle size measurements made with other measuring instruments could result in other measured values because of the non-spherical structure of the aggregates.[5,6]

For testing purposes, a high-energy milling described in Ref. [7] was used starting out from a standard dispersion.

### Coating Formulation and Media Evaluation

To examine glossy inkjet media (fumed silica), the following coating formulation was used and, within the given bounds, optimized to the substrate in terms of both processability and adhesion. Tests within one series were carried out with the same formulation: 100 parts dispersion (with respect to solids), 10–35 parts polyvinyl alcohol (Mowiol® 40-88, Kuraray Europe) 10% (with respect to PVA) cationic polymer (PDADMAC, Catiofast® CS, BASF) and deionized water up to the desired solids content of the coating formulation. Application by means of coating bar, and drying with hot air (blow dryer).

The corresponding applies to the matte coatings (precipitated silicas). Here however, completely saponified PVA (Mowiol® 28-99, Kuraray) was used and no cationic polymer.

The coating formulations were evaluated with a Brookfield-viscosimeter; solids content determination and pH value.

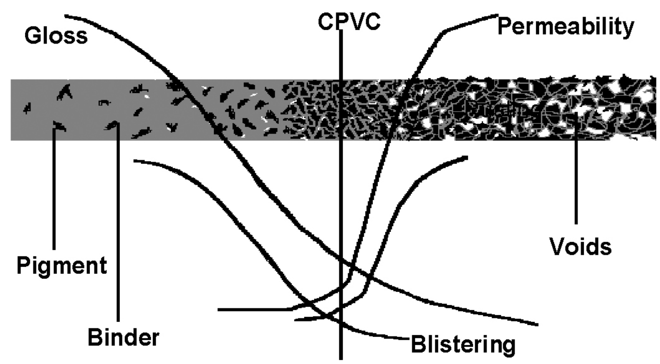


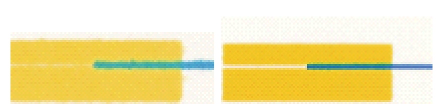

*Figure 4. Critical Pigment Volume Concentration (CPVC) and related parameters*[8]

The determination of the binder demand is fundamental to the quality determination of the precipitated silica. The determination was accomplished by using several coating formulations with increasing binder quantities to identify the optimum binder quantity that ensures surface strength while also keeping the binder demand low enough to retain an open-pore coating (see Figure 4).

PE film (glossy) or coated base paper with a grammature of 90 g/m² (matte) were used as substrates.

For glossy media, a gloss measurement was carried out at 20° and 60° Bragg angle using the method of Lehmann, and 5 duplicate measurements were made.The printers Epson Stylus Color 980 and Epson Stylus Photo 950 were the main printers used for the final inkjet print tests.

Image analysis was performed either visually, by trained personnel who applied different clearly defined criteria (see results), or automatically in the following way. The widths and roughnesses of the contact areas were measured with a digital microscope (PIAS; QEA/USA). These measurements were used to compute the values for bleeding and intercolor bleeding. These numbers show the effect of ink absorption most directly.



poor bleeding     very good bleeding

*Figure 5. Example of a printing pattern for PIAS measurements*

## Results and Discussion

### Gloss-Related Particle Parameters

Optimization of powder production and of the dispersion production itself were both undertaken when developing the dispersions for glossy inkjet media. Taking the dispersion AERODISP® WK 341 as an example, it is very easy to see what effect particle parameters have on the quality of the media that is produced.

During the development phase of this dispersion, some batches exhibited a certain coarse particle portion at around 10 µm during the particle size measurement, a result that correlates very well with measured gloss values of the layers (see Figure 7). Here it should be noted that the method of measuring particle size (static light scattering) over-emphasizes the coarse particles and can thus be used as a sensitive probe (see Figure 6). The actual concentrations of coarse particles at 10 µm are approximately an order of magnitude lower than the values of a few percent (100-Q<1µm) indicated here. Actual concentrations of less than 0.1% were determined using other methods (e.g., single particle counting).

The dispersion AERODISP® WK 341, which is being sold today, shows very high gloss values because of its low coarse portion. In formulating the coating formulation, it is necessary to take care that the interaction of anionic and cationic components does not cause reaggregation of the particles and an associated deterioration in the gloss.

Without using special processes to increase the gloss, another increase in the gloss values beyond 50 dots can still be achieved only by reducing the aggregate size in the fine portion. This reduction would come at the cost of a degradation in the image quality (see next section).

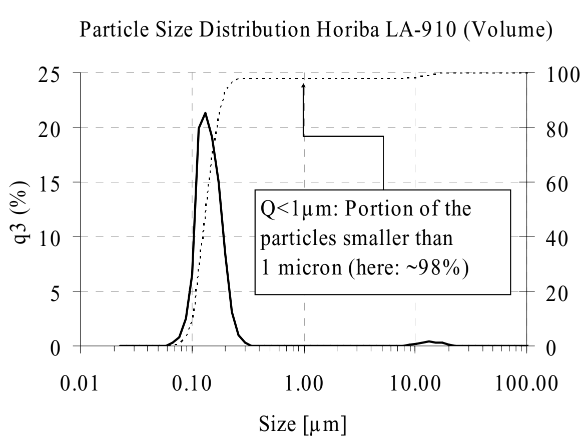



*Figure 6. Particle Size Distribution of a development sample of AERODISP® WK341 (not representing the actual product distribution). The use of static light scattering over-emphasizes the coarse particle portion.*

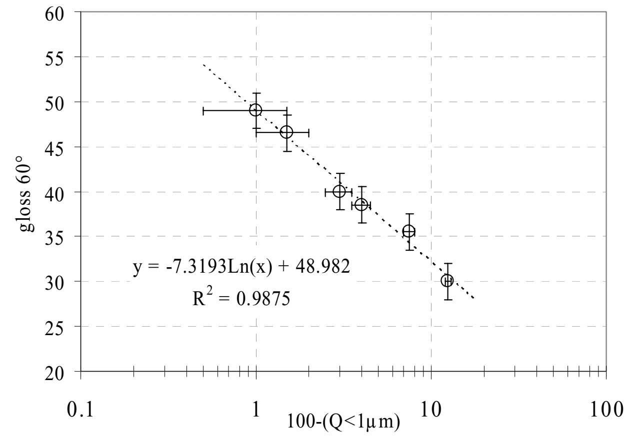



*Figure 7. Impact of the coarse particle portion on the gloss*

### Adsorption-Related Particle Parameters

The image quality that can be attained with microporous receiving layers in terms of resolution and color reproduction is basically determined by the pore volume and capillary structure of the layer. How well and how rapidly a layer is able to take up the liquid of the ink droplets is directly related to the structure and size of the aggregates.

Starting with the alumina dispersion AERODISP® W 630, which was internally used as a reference system for all other microporous systems in connection with the attainable quality, the aggregate size of the alumina particles was next reduced in three stages from approximately 130 nm down to 84 nm by means of high-energy milling.

The milling causes a drastic decline in the viscosity of the dispersion and the coating formulations produced from it. The gloss of the layers rises strongly, indicating that the particles can now be packed very well and that they consequently form compact layers that form only a few pores and capillaries.

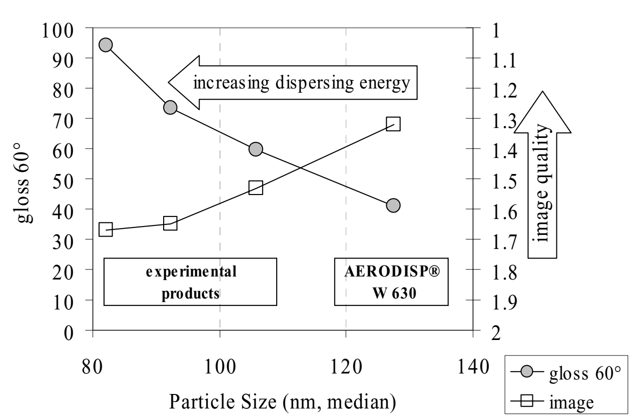



*Figure 8. Impact of the dispersing process on particle size, gloss and image quality (alumina dispersions at 30% solids content)*

Several trained personnel performed a visual analysis of the image quality in terms of the criteria color intensity (YCMK), dot sharpness, transitions (color in color, black in color), contours, characters, continuous tone, and photo quality, and evaluated each criterion according to a clearly defined grading scale from 1 (excellent) to 6 (very poor). Figure 8 shows the average values of these evaluations and the gloss values of this test series. The color transitions, dot sharpness and photo quality in particular contributed to the bad grades. These parameters are all closely connected to ink absorption, whereas contours, characters, and continuous tone all remained good and practically unchanged.

In the case of the silica for the matte inkjet coating, it is difficult to make a direct correlation of absorption properties with the physical data given in Table 2 because many other parameters as well as the formulation itself have a very great effect. A relationship between BET and the PIAS absorption data can be recognized in Table 3. The larger the specific surface of the powder, the consistently better the absorption properties corresponding to optimized inkjet media.

The same also applies to fumed silica (see Table 4), although there is insufficient space at this point to prove it in detail.

### Particle and Dispersion Properties and their Relation to the Processability of the Coating Formulation

In the development of microporous inkjet media, it is not only the attainable image quality that ultimately determines success, but also the processability of the coating formulation and other more economic aspects like the solids content of the coating formulation. In most cases it is necessary to fight trends in the opposite direction and find a compromise between technical and economic aspects. Whereas for example, the best image quality in terms of color reproduction and resolution can be achieved with particles of high surface, particles with smaller surface on the other hand permit large pigment/binder ratios, a feature that is desirable for economic reasons. As a supplier of raw materials for inkjet media, Degussa consequently sells different materials for different market segments.

Tables 3 and 4 and Figures 9 and 10 show the binder demand and attainable solids content for different products on the basis of model formulations based on PVA, each formulation having been optimized for its respective product.

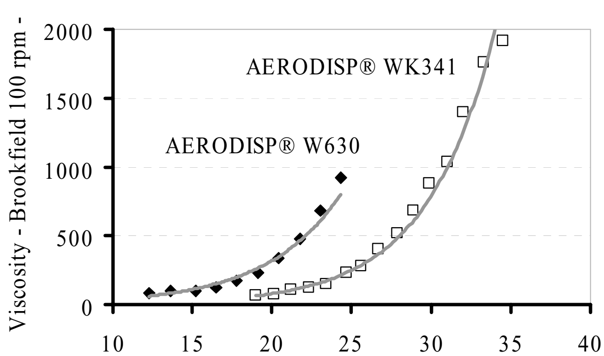



*Figure 9. Attainable solids content of the coating formulation with different dispersions of fumed particles*

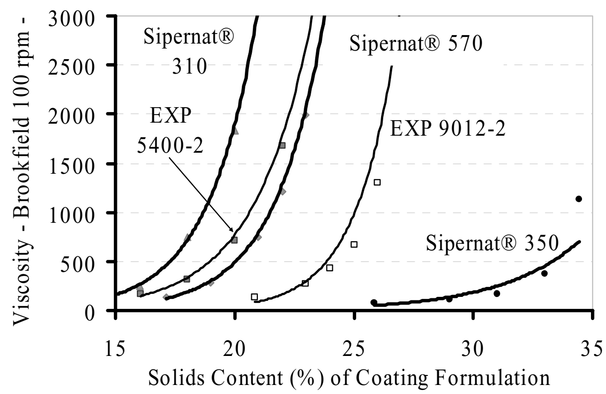



*Figure 10. Attainable solids content of the coating formulation with different SIPERNAT® particles.*

**Table 3. Absorption and Binder Demand of Precipitated Silica Types**

| | BET [m²/g] | Absorption acc. to PIAS-Normalization | Binder Demand (parts per 100 parts pigment) | Pigment/Binder Ratio |
|---|---|---|---|---|
| **Sipernat® 350** | 50 | 0.72 | 5 | 20.0 |
| **EXP 9012-2** | 175 | 1.00 | 15 | 6.7 |
| **EXP 5400-2** | 375 | 1.00 | 35 | 2.9 |
| **Sipernat® 570** | 750 | 1.05 | 25 | 4.0 |
| **Sipernat® 310** | 750 | 1.09 | 30 | 3.3 |

**Table 4. Binder Demand and Pigment/Binder Ratio of the Dispersions for Glossy Media**

| Binder Demand **(parts per 100 parts dry pigment)** [Pigment/Binder Ratio] | AERODISP®. WK 341 | Experimental Dispersion, BET ~130 m²/g | AERODISP® W 630 |
|---|---|---|---|
| on PE-film | 11 [9:1] | 37 [2.7:1] | 23 [4.4:1] |
| on precoated paper (e.g., matte paper) | 7 [14.3:1] | unk. | 12 [8.3:1] |

## Conclusions

This article attempts to show fundamental relationships between physical-chemical parameters of the pigments and the properties of the inkjet media based on these parameters.

In the glossy media sector, we used dispersions of fumed particles in which the particles have a cationic surface charge (important for ink fixation and water fastness) and form interparticular voids and capillaries, properties that are essential for adsorption and image characteristics. We have shown that changes to the aggregate structure directly affect media properties like absorption and gloss.

The matte media sector makes use of SIPERNAT® particles with particle sizes of several µm. Their performance in terms of absorption and image quality is basically determined by their internal pore structure.

We have also discussed important general economic conditions that are important for the development of inkjet media like binder demand and attainable solids content of the coating formulations.

All statements that we have made were based on simple model formulations based on PVA. These model formulations have already produced major results, but do not come anywhere close to covering all the possibilities. Manufacturers of inkjet media can exploit further potentials of the pigments, in particular by utilizing more sophisticated formulations (other binders, etc.) and by a multi-layered structure of the media. As a supplier of raw materials who is actively involved in the technological development, we are convinced that the still remaining technical challenges of microporous inkjet media can be solved soon.

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3. The term "aggregate" is used in the sense of DIN 53206 for a collection of primary particles that have tightly intergrown together. "Agglomerates," in contrast, are only loose combinations of aggregates and/or primary particles. The terms aggregate and agglomerate are used in the reverse sense in English-speaking countries. See the discussion of these terms in Kaye, B.H., Characterizing Powders and Aerosols, Wiley-VCH, Weinheim (1999).
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## Biography

**Dr. Christoph Batz-Sohn** studied chemistry and recieved his Ph.D. in organometallic chemistry at the University of Bielefeld in 1996. In 1997 he joined Degussa working as a research chemist in the field of functional silanes. Since 2000 he has been working as a team leader for the development of tailor-made silica and alumina dispersions for different application areas. His main interest belongs to glossy inkjet coatings. He holds several patents in the fields of silanes, dispersions and their applications.