Novel Sub-Micron Silica Gels for Glossy, Ink-Receptive Coatings

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Abstract

Advances in ink-jet printing technology have enabled the output of digital images that rival the quality of images produced on photographic film. As a result, there is demand for ink-jet media with intermediate and high gloss finishes, so that the ink-jet printed image resembles a photographic image. Coated ink-jet media are necessary to produce the desired glossy image characteristics. Existing coating technologies can be divided into those that are resin rich, and those that are pigment rich. The latter coatings are microporous as a result of the packing of small, inorganic particles. A key ingredient used widely in both types of systems is amorphous silica, which imparts many desirable characteristics to the coating and final image.

We report here novel submicron-sized materials, based on amorphous silica gels, that can be used to prepare high capacity ink-receptive coatings that also exhibit gloss finishes. As a result of their internal porosity, the materials can be used to produce coatings with substantial void space for liquid absorption. As a result of their small particle size, the materials can be used to produce films of relatively high gloss, even in a pigment rich coating film. These new materials should play an integral role in the development of coated, glossy media for high productivity ink-jet printers.

Introduction

The number of color ink-jet printers installed in homes and businesses is growing rapidly, and in order to produce high-quality color images with those printers, specialty media are required. One of the key current drivers of the specialty media market is the emergence of ink-jet printing devices capable of delivering photo-quality images. The imaging media strongly influences quality attributes of the final images such as color gamut, image resolution, and gloss. While the quality of the output of these devices has increased, so has the desire to utilize them more productively; that is, to generate images faster. Media also play a strong role in printer productivity, because of the time necessary for the ink liquids to dry.

There are many different coating formulations and technologies for the preparation of glossy ink-jet media. Two basic types of systems exist, those that are resin-rich and those that are pigment rich. Resin-rich systems typically contain water swelling polymers such as gelatin, poly(vinylalcohol) (PVOH), and poly(vinylpyrrolidone) (PVP).[1] Another type of resin system involves a small amount of colloidal alumina dispersed in a hydroxypropyl-cellulose/PVOH matrix.[2] These systems absorb ink-liquids by a film swelling mechanism, not by evaporation or containment of liquid in pores. Pigment rich systems, that is, those formulated above the critical pigment volume concentration, include those that are composed primarily of amorphous silica,[4] and/or alumina.[3] In these systems, a porous network exists for the absorption of ink-fluids.

There are several types of amorphous silicas, including fumed, colloidal, precipitated and gel.[5] Silica gel is unique compared to the other types of silicas because of its well-defined, internal porous network, with pore diameters less than about 600Å This internal pore structure is of key functional utility in ink-jet coatings with regard to both image quality and drytime. To date, silica gel materials have been supplied commercially as powders with median particle size greater than about 4 µ, and these are used widely in matte coated ink-jet media.

The gloss of a film depends on the reflection of light by the film surface.[6] Pigments dispersed within a film affect gloss by contributing to surface roughness (roughness lowers gloss by the scattering of light) and by influencing the refractive index of the film. Thus, in order to obtain high gloss finishes, the surface must be very smooth. The surface roughness of films formulated above the critical pigment volume concentration is determined by particle size, shape and size distribution. For pigment rich films to have high gloss, the pigment particle size must therefore be relatively small.

Porosity in Dried Silica Films

The absorptive capacity of an ink-receptive film depends either on the ability of the film to swell and chemically bind the liquid, or on the available void space in the film to absorb and contain the liquid, or on a combination of the two. For a film composed of non-porous particles only, the void space depends on the packing arrangement of the particles, and a typical void fraction for the relatively dense packing of such a system of particles is 0.35. Particles of colloidal silica are non-porous, and the silica itself has a particle density of 2.2 g/cc. The calculated total volume occupied by such dense-packed particles is 0.70 cc/g (void volume = 0.24 cc/g), and the density of a dried film is 1.4 g/cc. Table 1 shows void volumes, measured by N_2 porosimetry (at $p/p_o = 0.967$) for dried films of commercially available, spherical colloidal silicas, which shows that the void volumes are ~0.2 cc/g, in good agreement with the calculated value. Also shown in the Table is the porosity of a dried film of commercially available fumed silica, and the value of 0.33 cc/g is again in good agreement with the value of 0.24 cc/g calculated for relatively dense packing of particles.

Particle shape obviously influences the void volume of a dried film as well, and non-spherical, ("pearl-like") colloidal silicas are commercially available. One of the ideas behind potential use of these materials in ink-jet coatings is that the void volume in a dried film comprised of such particles will be greater than that comprised of the spherical particles. Also shown in Table 1 are the void volumes for some non-spherical, colloidal silicas, and these are in the 0.4-0.5 cc/g range. Thus, the non-spherical geometry for these particles does give a more open particle packing arrangement, corresponding to a void fraction of 0.5.

Table 1. Void Volumes for Various Dried Silicas.

Type	Part. Size (nm)	pH	Void Vol.* (cc/g)	Surf. Area (m^2/g)
Spherical Colloidal				
SC-A	15	10	0.17	161
SC-B	77	9.6	0.20	28
Pearl-Like Colloidal				
PC-A	127x20	5.7	0.53	91
PC-B	125x45	5.5	0.40	59
Fumed				
F-A	200	8.4	0.33	49
Silica Gel				
3U	300	8.5	0.74	216
3SY	300	8.2	0.79	226

*Drying Conditions: 105C for 1.5 hr;

Void volumes are pore volumes measured by N2 porosimetry

By comparison to the above materials, particles of silica gel are internally porous, and the internal porosity of typical commercial grades can vary over a range from 0.4 to 2.1 cc/g. 1.0 cc/g is a typical pore volume for these materials. The total calculated volume occupied by such particles packed together (with an interparticle void fraction of 0.35) is 2.2 cc/g (total void volume, corresponding to interparticle and internal porosity, is 1.77 cc/g), and the density of a dried film comprised of such particles is calculated to be 0.65 g/cc. It can be seen that the internal porosity of the silica gel contributes significantly to the total void volume.

The porosity in a film of packed silica gel particles depends on several factors. One consideration is the size of the internal particle pores compared to the particle size of the silica. The average pore size of a silica gel is related to the pore volume and surface area through the relationship

$$D = 40{,}000 * V/SA \tag{1}$$

where D is the average pore diameter in Å, V is the pore volume in cc/g, and SA is the surface area in m^2/g. For a 300 m^2/g silica gel with 1.0 cc/g pore volume, the average pore diameter is 130ÅAt one extreme, when the particle size of the silica gel approaches the pore diameter, the internal porosity is obviously lost. Thus, a practical lower limit for the particle size of a porous silica gel particle with the above surface area/pore volume is about 50 nm. Based on models of the silica gel pore structure as various arrangements of cylindrical pores, it is possible to arrive at the conclusion that particles that are roughly ten times the size of the pores will exhibit roughly a 30% lower internal void volume compared to a comparable particle that is 1000 times the size of the pore diameter.

A second consideration that affects the void volume of any dried, porous network is the amount of shrinkage that occurs during the drying process.[7] As the liquid meniscus recedes within the pores, capillary and adsorption forces oppose the exposure of the solid phase. The capillary pressure or tension that the receding liquid exerts on the solid leads to compression of the solid, resulting in shrinkage, and is related to the pore diameter and the solid-liquid and solid-vapor surface tensions. Finally, it is well known that for silica gels, the final dried porosity also depends on factors such as the drying rate, liquid pH and the effect of chemical additives on the silica gel surface.[8]

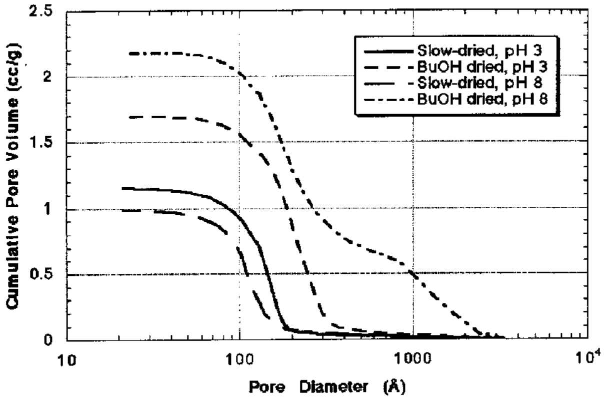

Figure 1. Nitrogen Porosimetry of a Silica Gel Dried under Various Conditions

Shown in Figure 1 are cumulative pore volume curves for a 1.8μ silica gel slurry dried under various conditions. The silica gel sample dried slowly from butanol slurry at pH 8 exhibits a total pore volume of 2.2 cc/g. From the curve for this sample, it can be seen that there is a porous network internal to the particle at about 160 Å and another porous network typical of interparticle pores at about 1000 Å. The same sample, when dried slowly from aqueous slurry at pH 8, exhibits a pore volume of 1.0 cc/g, with an average intraparticle pore diameter of roughly 100 Å. Shown in Table 1 are some data for a 0.3μ silica gel, demonstrating that the void volume when dried from aqueous solution at pH 8 is about 0.8 cc/g, considerably higher than the colloidal and fumed silicas.

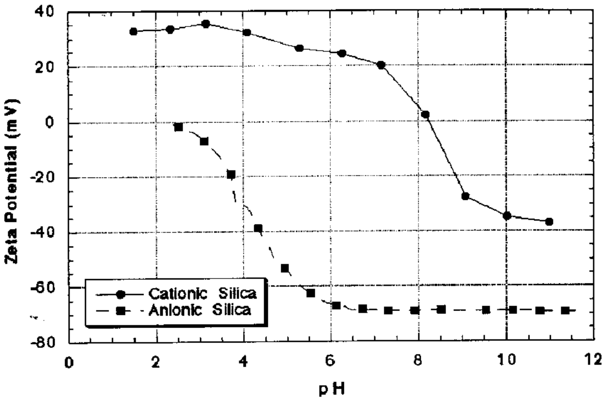

Figure 2. Zeta Potential of Unmodified and Modified Silica. (See Ref. 9)

Colloid Stability/Formulation Compatibility

Particles dispersed in aqueous solution usually develop a surface charge which can be measured and reported as the zeta potential (mV). For electrostatically stabilized sols, the magnitude of the charge affects the sol stability so that higher charge results in a more stable sol. Hydroxyl groups on the surface of silica are somewhat acidic, and deprotonate as a function of pH. The otherwise unmodified surface is thus negative over the pH range of most coating formulations. This charge can be reversed by adsorption or chemical modification of the silica surface. Figure 2 shows zeta potential measurements as a function of pH for an unmodified silica surface (referred to as “anionic”) and a modified, submicron silica gel, (referred to as “cationic”).
In addition to the influence of zeta potential on aqueous sol stability, the surface charge also strongly affects the interaction of the silica with other components in a coating formulation, which often contain ionic polyelectrolytes such as poly(ethyleneimine) and poly(diallyldimethylammonium chloride) as dye mordants. Thus, it is desirable to develop cationic submicron silica gels, as well as anionic submicron silica gels, in order to allow compatibility with many types of coating formulations.

Silica-Based Ink-Receptive Coatings

Ink-jet coating formulations were prepared with 0.3μ median particle size silicas, the formulas were coated onto PET film (Mellinex 534) and the performance of those coatings was evaluated. Shown in Table 2 are data for films prepared by deposition of a 100μ wet film of 15% total solids coating formula comprised of various anionic silicas and PVOH in the ratio silica:PVOH 70:30. The densities of the films prepared using 0.3μ silica gels were in the 1.2 to 1.3 g/cc range, while that prepared from traditional colloidal silica was 1.9 g/cc. Thus, the silica gel porosity gives rise to a substantial increase in total coating porosity compared to the same film prepared with a non-porous silica.

Table 2. Ink-Receptive Film Density for Various Silicas

Silica	Film Thickness (μ)	Coat Weight (g/m^2)	Coat Density (g/cc)
Silica Gel 3U	13.0	16.90	1.30
Silica Gel 3SY	9.3	17.10	1.22
Colloidal Silica SC-B	14.0	17.80	1.91

Another set of coating formulations were prepared with anionic and cationic, 0.3μ silica gels. These formulations were also silica rich (silica:resin 63:37), while the resin component consisted mostly of PVOH. Shown in Figures 3 and 4 are electron micrographs for the anionic and cationic coating formulations, respectively, at 1K and 20K magnifications. It can be seen that the coatings are highly uniform and defect free. From the higher magnification images, it is observed that the surface roughness is related to the silica gel particle size, although there is clearly evident a secondary structure with larger domain size than the actual particle size. Thus, while particle size does impact the gloss of the coating, other factors affect the smoothness of the film during drying as well. The gloss of these coatings is reported in Table 3. It can be seen that the 60° gloss varies from 18 to 34 and the 85° gloss varies from 82 to 89, so that these coatings are considered to have a satin finish.

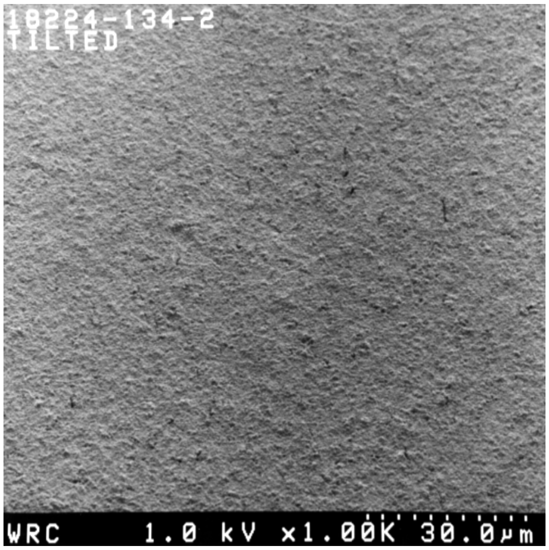

Figure 3a. SEM Micrograph of Anionic, 0.3μ Silica Gel Coating Formulation at 1000K.

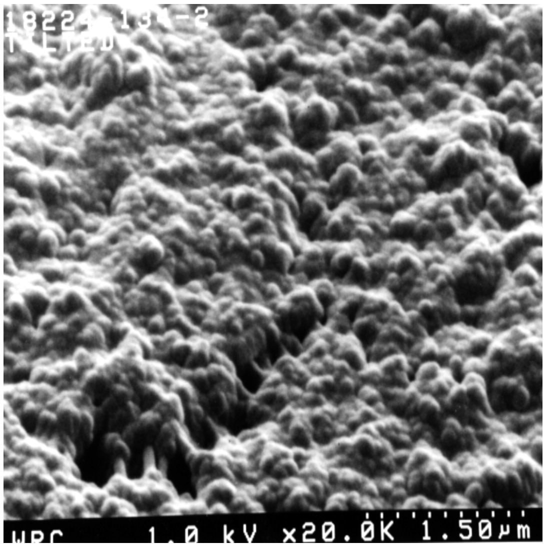

Figure 3b. SEM Micrograph of Anionic, 0.3μ Silica Gel Coating Formulation at 20,000K.

Table 3. Gloss of Coatings Based on 0.3 Micron Silica Gel

Silica	Gloss		
	20	60	85
Silica Gel 3U	3	18	82
Silica Gel 3CS	9	34	89

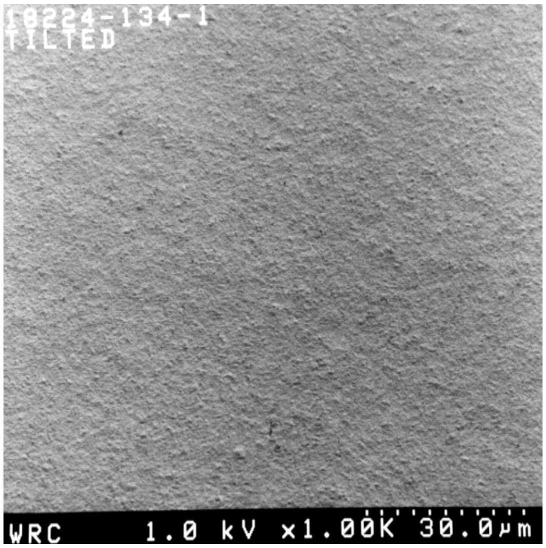

Figure 4a. SEM Micrograph of Cationic, 0.3μ Silica Gel Coating Formulation at 1000K.

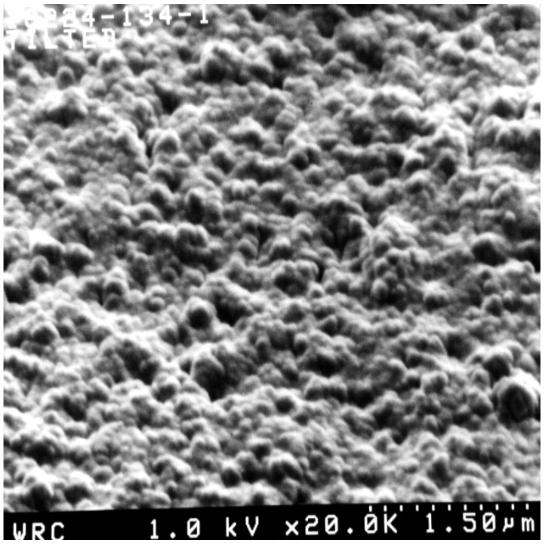

Figure 4b. SEM Micrograph of Cationic, 0.3μ Silica Gel Coating Formulation at 20,000K

Table 4. Effect of Film Thickness on Gloss

Wet-Film (μ)	Gloss		
	20	60	85
12	4	18	79
24	4	17	78
36	3	17	77
60	3	17	79
100	2	16	79

The effect of film thickness on gloss was also measured for films of anionic, 0.3µ silica gel prepared from the composition silica:resin 67:33, with PVOH as the main resin component, at 15% total solids. Results, in Table 4, demonstrate that over the range of wet films of 12 to 100 µ, there is essentially no variation in gloss with film thickness.

Table 5. Effect of Silica Gel Particle Size on Gloss and Surface Roughness

Particle Size (µ)	Gloss			Surface Roughness Rq (nm)
	20	60	85	
1.0	2	3	35	671
0.7	2	4	57	527
0.3	5	20	78	217

The effect of the median particle size of the anionic silica on surface roughness and gloss of coated films was examined using optical profilometry. Root-mean square (R_q) surface roughness values were measured for three different regions for each coated film, and average values are given in Table 5, along with gloss values for the films. It can be seen that both the surface roughness and gloss are monotonic functions of the silica gel particle size.

Conclusions

Novel submicron silica gels, either with negative or positive zeta potentials in aqueous solution, have been prepared and characterized. When aqueous suspensions of the particles are dried, the solid exhibits porosity characteristic of the internal porosity of the silica gel material itself. As a result, it is shown that dried films of silica gel exhibit lower density and higher porosity than dried films of other types of commercially available, sub-micron silicas.

Similarly, when these silicas are incorporated into coatings formulated above the critical pigment volume concentration, dried silica gel/resin films exhibit lower density and higher porosity than those composed of non-porous silicas.

The effect of silica gel particle size on surface roughness and gloss of coating formulations was evaluated. Particles with median size of 0.3µ can be used to produce intermediate gloss coatings (20-30 gloss at 60°) in a pigment rich system. These coatings also exhibit excellent ink-jet printability and rapid drytime.

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Biography

David Chapman received his B. S. degree in chemistry from St. Lawrence University in New York in 1980 and a Ph.D. in Inorganic Chemistry from the University of Tennessee, Knoxville, in 1984. From 1984 to 1987, he worked in the Molecular Sieves Department of the Union Carbide Corporation at Tarrytown, NY. From 1987 to the present, he has worked at W. R. Grace in Columbia, Maryland. His work has focused on silica gels and their industrial applications, including their utility in ink-receptive coatings.