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Novel Silica Gels for Glossy, Ink-Receptive Coatings

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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.

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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 absorb and hence 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).[1,2] Another type of resin system involves a small amount of colloidal alumina dispersed in a hydroxypropylcellulose/PVOH matrix.[3,4] 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,[5,6] and/or alumina.[7] 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.[8] 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 μm, 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.[9,10] 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.

Experimental

The silica materials utilized in these studies were either obtained commercially, or were produced as disclosed in the patent literature.[11] Commercial colloidal silicas were from Nissan Chemical (Snowtex -40; Snowtex-2L; Snowtex PS-M; Snowtex PS-L) and fumed silica was from Degussa (OX-50). Polyvinyl alcohol (PVOH, Airvol 523) was obtained from Air Products. Silica surface modification and preparation of ink jet

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TABLE I. Calculated Void Volumes for Various Particle Arrangements

Interstital	Particle Porosity?	$V_{interstitial}$ (cm^3/g)	V_{pore} (cm^3/g)	$V_{total\ void}$ (cm^3/g)
No	No	0.00	0.00	0.00
Yes	No	0.24	0.00	0.24
No	Yes	0.00	0.80	0.80
Yes	Yes	0.67	0.80	1.47

coatings were carried out according to examples in the patent literature.[12] Silica porosity was determined using nitrogen porosimetry after the samples were dried slowly at 105°C at their native pH for 1.5 h, and then were activated under vacuum at 105°C. Silica particle size was obtained using a Horiba LA-900 Light Scattering Analyzer with deionized water as the solvent. Zeta Potentials were measured using a Malvern Zetasizer 3000 HS, with high purity water (Milli-Q deionized water) as solvent, and dilute hydrochloric acid or sodium hydroxide to adjust pH. Coating formulations were prepared with 0.3 µm median particle size silica gels with PVOH. The formulas were coated onto PET film (Mellinex 534) with a 100 µm wet film of 15% total solids. Film thickness was measured with a Fischer Isoscope MP30. Coating density (and hence volume) was calculated from coat weight and thickness data, and coating void volumes were calculated by subtracting the additive volumes of the pure coating components from the calculated coating volume. Gloss measurements were made using a BYK-Gardner micro-TRI-glossmeter. Surface roughness was measured using a Wyko Surface Profiler at 49X magnification, based on the technique of vertical scanning interferometry.

Results and Discussion

Porosity in Dried Silica Films

The absorptive capacity of an ink-receptive film depends 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. The void volume in a film of packed particles depends on the interstitial void volume and the particle pore volume. For coating films formulated below the critical pigment volume concentration (CPVC), the interstitial void volume is negligible. In Table I are calculated void volumes for an arrangement of particles that are either non-porous or porous, and which have either no interstitial void volume, or are packed with a void fraction of 0.35. It can be seen that particles with an internal porosity of 0.8 cm^3/g, when packed in an arrangement with interstitial void fraction of 0.35 give a resultant total void volume of 1.47 cm^3/g.

In Table II are void volumes and surface areas, measured by N_2 porosimetry (at $p/p_o = 0.967$) for dried films of various silica types with particle size less than 1 µm. Also included in Table II are calculated geometric surface areas based on the smallest particle dimension quoted. Spherical colloidal silica films exhibited void volumes of ~0.2 cm^3/g, in good agreement with the calculated value shown in Table I. Also shown in the Table II is the porosity of a dried film of commercially available fumed silica that was wet-milled to 0.2 µm, and the value of 0.33 cm^3/g is again in reasonable agreement with the value of 0.24 cm^3/g calculated for relatively dense packing of particles. For the spherical colloidal and fumed silicas, it can be seen that the measured surface areas are in good agreement with the calculated geometric surface areas based on non-porous, dense phase silica.

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 II are the void volumes and surface areas for some non-spherical, colloidal silica. The void volumes are in the 0.4-0.5 cm^3/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. The measured surface areas are in good agreement with the calculated geometric surface areas using the smallest particle dimensions quoted, consistent with non-porous, dense phase silica particles.

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 cm^3/g. As shown in Table II, the measured void volume for such particles is ~0.8 cm^3/g, and the surface areas are >200 m^2/g. Thus, the void volumes for the silica gel films are greater than those for the other silica types. Also, it can be seen that the measured surface areas are vastly greater than that calculated for 0.3 µm particles (the measured particle size for these samples), a manifestation of the fact that the silica gel particles are internally porous.

The measured pore volumes for the silica gel samples is less than the calculated value based on a pore volume of 0.8 cm^3/g (1.47 cm^3/g; see Table I), and is less than the pore volume for comparable silica gel samples of larger size. Based on pore size distributions, it is be-

TABLE II. Void Volumes and Surface Areas for Various Dried Silicas

Type	Particle Size (nm)	pH	Void Vol. (cm^3/g)	Surf. Area (m^2/g)	Calc. Surf. (m^2/g)
Snowtex –40	15	10	0.17	161	195
Snowtex –2L	77	9.6	0.20	28	35
Pearl-Like Colloidal					
Snowtex PS-M	127 × 20	5.7	0.53	91	136
Snowtex Ps-L	125 × 45	5.5	0.40	59	68
Fumed					
Milled OX-50	200	8.4	0.33	49	14
Silica Gel					
3U	300	8.5	0.74	216	9
3SY	300	8.2	0.79	226	9

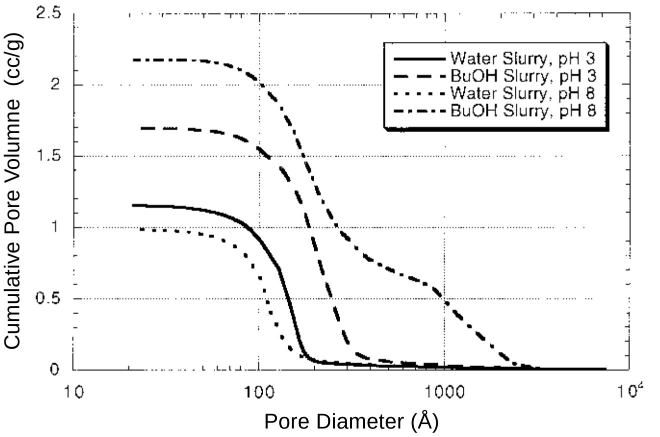


Figure 1. Nitrogen porosimetry of a silica gel dried under various conditions.

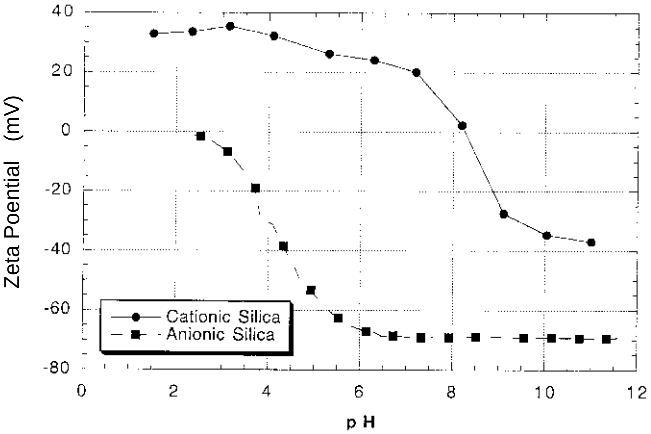


Figure 2. Zeta Potential of Unmodified and Modified Silica. (See Ref. 15)

lieved that the ~0.8 cm^3/g represents particle pore volume, and that the interstitial void volume is negligible. In order to account for the disparity between the measured and calculated void volumes for the dried silica gel samples, it is necessary to consider the effects of particle size and shrinkage on porosity. With regard to the effect of size on porosity, it is noted that when the particle size of the silica gel approaches the pore diameter, the internal porosity obviously becomes negligible. The average pore size of a silica gel is related to the pore volume and surface area through the relationship

$$D = 40{,}000 * V/SA \qquad (1)$$

where D is the average pore diameter in Å, V is the pore volume in cm^3/g, and SA is the surface area in m^2/g. For a 300 m^2/g silica gel with 1.0 cm^3/g pore volume, the average pore diameter is 130Å. 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.[13] As the liquid meniscus recedes within the pores, capillary and adsorption forces oppose the formation of a solid-gas interface. 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.[14]

In order to illustrate the effect of shrinkage on porosity, pore volumes were measured by nitrogen porosimetry for a very low density, ~2 μm silica gel slurry dried under various conditions (Fig. 1). The silica gel sample dried slowly from butanol slurry at pH 8 exhibits a total pore volume of 2.2 cm^3/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 cm^3/g, with an average intraparticle pore diameter of roughly 100 Å. These data show the effect of the different compressive forces during drying on the porosity of the dried network. It is also noted from the figure that pH has an effect on the final porosity, such that the sample dried from water at low pH has slightly higher pore volume than that dried from water at high pH.

Colloid Stability/Formulation Compatibility

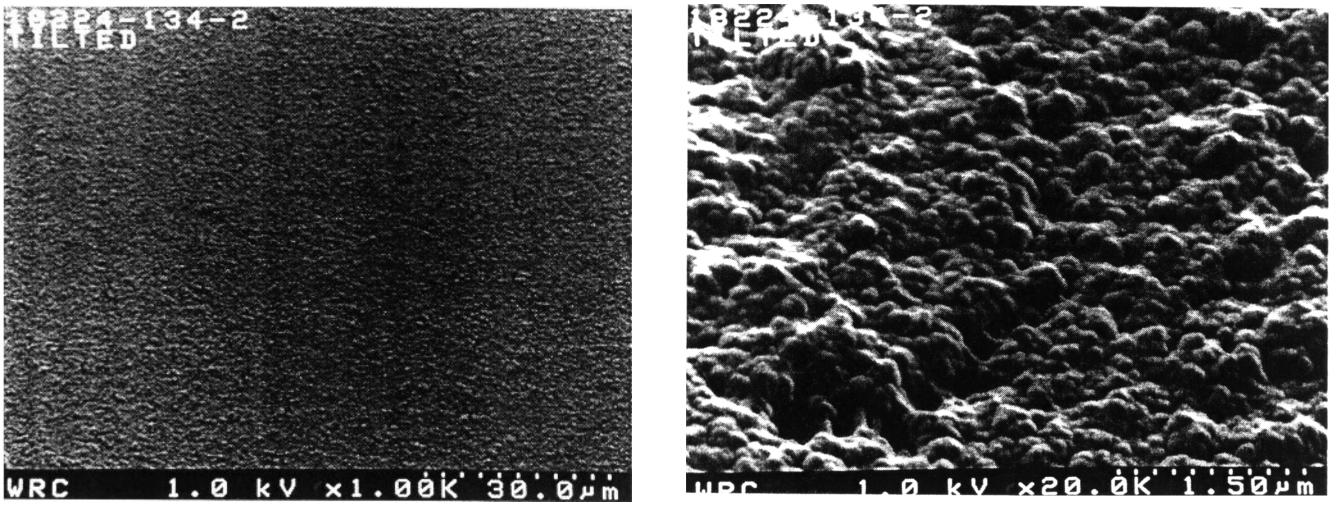
Particles dispersed in aqueous solution usually develop a surface charge that can be measured and reported as the zeta potential (mV). For electrostatically stabilized sols, the magnitude of the charge affects the sol stability so that higher charge results in a more stable sol. Hydroxyl groups on the 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, and is referred to as “anionic”. Adsorption or chemical modification of the silica surface can reverse this charge, and the resulting material is 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, that often contain ionic polyelectrolytes such as poly(ethyleneimine) and poly(diallyldimethyl-ammonium 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.

Figure 2 shows zeta potential measurements as a function of pH for an unmodified silica surface and a cationic, 0.3 μm silica gel prepared according to the patent literature.[12] It can be seen that the isoelectric point for the “cationic” silica gel is near pH 9. Qualitatively, it was found that coating formulations containing PVOH and the “anionic” silica gel were stable towards particle agglomeration so long as the pH was above ~7. Also, coating formulations containing “cationic” silica gel in combination with PVOH and polyelectrolytes (e.g., those containing quaternary nitrogen) were stable towards agglomeration, so long as the pH of the system was below ~6.

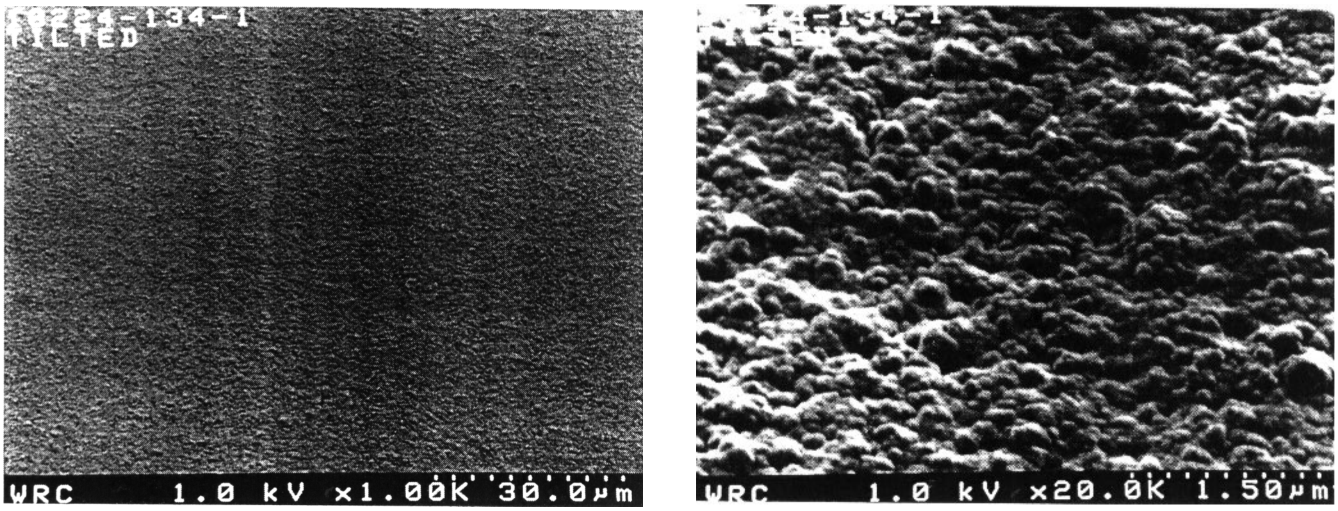
TABLE III. Ink-Receptive Film Densities and Calculated Void Volumes for Various Silicas

Silica	Film Thickness (μm)	Coat Weight (g/m^2)	Coat Density (g/cm^3)	Calc. Void Vol. (g/cm^3)
Silica Gel 3U	13.0	16.90	1.30	0.22
Silica Gel 3SY	14.0	17.10	1.22	0.27
Colloidal Silica Snowtex 2L	9.3	17.80	1.91	0.00



(a) (b)

Figure 3. (a) SEM micrograph of anionic, 0.3 μm silica gel coating formulation at 1,000X. (b) SEM micrograph of anionic, 0.3 μm silica gel coating formulation at 20,000X.



(a) (b)

Figure 4. (a) SEM micrograph of cationic, 0.3 μm silica gel coating formulation at 1,000X. (b) SEM micrograph of cationic, 0.3 μm silica gel coating formulation at 20,000X.

Silica-Based Ink-Receptive Coatings

Simple films were prepared using 0.3 μm anionic silica gels, and mixed with PVOH in the proportion 70:30 silica:PVOH. For comparison, a film was also prepared using colloidal silica. The densities of the films prepared using 0.3 μm silica gels were in the 1.2 to 1.3 g/cm^3 range (Table III), while that prepared from traditional colloidal silica was 1.9 g/cm^3. The calculated void volume of the films containing silica gels were in the range of 0.2 to 0.3 cm^3/g, while for the colloidal silica, the calculated void volume was zero. Thus, the silica gel porosity gives rise to an increase in total coating porosity compared to the same film prepared with a non-porous silica. The values for the calculated void volumes for films containing both types of silicas are low considering the high silica content of the films. It is likely that the PVOH binder dries into a relatively dense phase, and fills the interstices between particles.

Another set of coating formulations was prepared with anionic and cationic, 0.3 μm silica gels. These formulations were also silica rich (silica:resin 63:37), while the resin component consisted mostly of PVOH. Shown in Figs. 3 and 4 are electron micrographs for the anionic and cationic coating formulations, respectively, at 1, 000 X and

TABLE IV. Gloss of Coatings Based on 0.3 μm Silica Gel

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

TABLE V. Effect of Film Thickness on Gloss

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

20,000 X 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 topography 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 as well. The gloss of these coatings is reported in Table IV. 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.

The effect of film thickness on gloss was also measured for films of anionic, 0.3 μm silica gel prepared from the composition silica:resin 67:33, with PVOH as the main resin component, at 15% total solids. Results, in Table V, demonstrate that over the range of wet films of 12 to 100 μm, there is essentially no variation in gloss with film thickness. While the gloss of the substrate is high, these coatings are relatively opaque so that the gloss of even relatively thin coatings is determined primarily by the surface roughness.

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 VI, along with gloss values for the films. It can be seen that the surface roughness and high angle (85°) gloss are monotonic functions of the silica gel particle size. However, the lower angle (20° and 60°) gloss values are not monotonic functions of silica gel particle size.

Conclusions

Novel 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 solids exhibit 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 with high pigment content, the 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 0.3 μm 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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