Silica Pigment Porosity Effects on Color Ink jet Printability

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Abstract

It is well known that the pore structure of a pigment can have a dramatic influence on the performance the pigment has in its end use application. Synthetically produced silica pigments can be manufactured with widely varied pore sizes and distributions. Although several technologies are included to give the broadest range of pore sizes, all are being used alone or in combinations in specialty paper coatings. The commercial ink jet application relies on synthetic silica pigments to deliver the proper combination of physical and chemical properties. The optimum combination of properties will deliver a print with good dot quality and excellent color production.

This paper will detail some of the impact that variations in pigment porosity have when the pigment is incorporated into a simple color ink jet coating. The effect of pore size and distribution on color density and dot formation characteristics will be discussed. It required the right combination of equipment, consumer interest and cost to bring ink jet printing to where it is today. There has over the past four years been an overwhelming increase in interest in ink jet printing. The major factor driving this has been the demand for high quality color in both home and office use as well as in sophisticated graphic arts applications. There have been a variety of new papers and new grades of paper marketed to capture specific portions of this growing demand.

Introduction

Although the manufacturers of commodity grades of paper are just now becoming aware of the benefits of highly structured pigments such as synthetic silicas and aluminas, specialty coaters have been using them for a number of years. The most widely used specialty structured pigment is synthetic silicon dioxide or silica pigments.

Silica pigment is a generic term used to describe a variety of naturally occurring as well as synthetically produced materials whose composition is essentially SiO_2. Silicon dioxide, SiO_2, is a compound that is present in 60% of the earth's crust and a key portion of mineral fillers such as kaolin and talc.[1] In its most abundant form, sand or quartz, it is a dense and non-porous material that is of little value as a pigment. Silica pigments that are produced commercially are chemically identical to their natural counterparts, yet are amorphous or unordered in structure. Amorphous silica pigments are very different from their natural counterparts and have become very useful to papermakers as well as specialty coaters.

Commercial Silica Production

Synthetic amorphous silica pigments are produced commercially in four distinct forms: Silica sols, pyrogenic or fumed silicas, silica gels and precipitated silicas. Producers of specialty papers are interested in the pigmentary forms. Fumed silica is the oldest commercial method to produce an amorphous silica pigment. It was developed by Degussa in 1941 in an effort to produce white carbon black as a reinforcing pigment. It involves the reaction of silicon metal and gaseous dry hydrochloric acid to form silicon tetrachloride. This is burned at 1000ºC to produce and condense a high purity silica pigment.

Fumed Silica Process

$$SiCl_4 + 2H_2 + O_2 + 3.76N_2 \xrightarrow{1000^{o}C} SiO_2 + 4HCl + 3.76N_2$$

Looking with more detail at the microporosity of the materials some distinct differences between the types of silica pigments become obvious. Fumed silica pigments have little or no internal micrporosity. The pyrogenic process forms fine droplets of liquid silica that stick to one another to form solid aggregates and clusters. These clusters are solid and non-porous. The fumed silica is a very fine particle size product with high levels of microporosity. Particle size in the range 10 - 30 μm is typical.

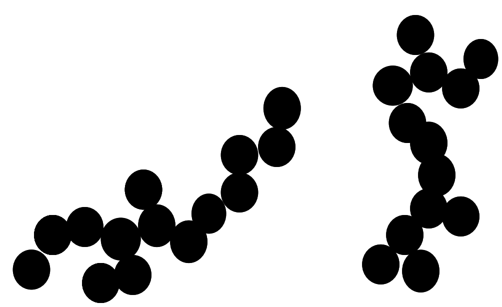

Figure 1. Illustration of fumed silica agglomerate particle chains

Liquid Silica Process

The other processes utilized commercially are liquid processes. The precipitation process reacts an alkali liquid silicate, waterglass, with a mineral acid such as sulfuric acid to form a solid precipitated pigmentary silica pigment. The silica gel process reacts the same waterglass with mineral acid under acidic conditions to produce a three dimensional solid silicon dioxide network that can be broken down into a pigmentary material.

$$Na_2O{:}3.3SiO_2 + H_2SO_4 \rightarrow 3.3SiO_2{:}H_2O + Na_2SO_4$$

All these processes yield amorphous pigments composed of silicon dioxide, yet are very different in their properties and their functionality's.

The Silica Gel Process

The gel process forms a cage-like structure that is up to 75% water. The way in which the product is dried determines the type of gel. Comparing the gel products we typically see larger particle sizes determined by mechanical size reduction and classification. Particle shape is considered to be irregular. Think of breaking a large piece of Jell-O[2] gelatin into smaller pieces. The particles will not take on any specific shape. The macro pore volumes are lower at 60 to 75 cc/100g. Pigment surface area, however; is very large, typically between 200 - 700 m^2/g[3].

Silica gel pigments tend to be very porous materials. The pore structure is controlled by the washing and drying conditions employed. The cage-like particles are full of water. As this water is removed the particles tend to collapse due to surface tension forces.[4]

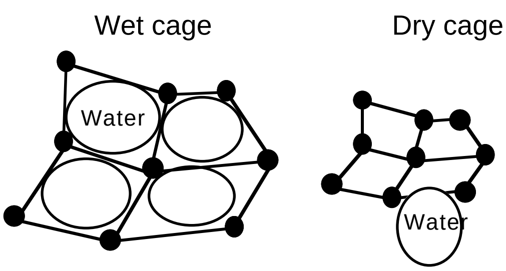

Figure 2. Illustration of gel particle shrinkage upon drying

Generally, silica gel products have a high degree of fine mesoporosity or microporosity as is evidenced by the high specific surface areas. The pores that are present are tightly distributed. The surface of these water-borne particles are populated with hydroxyl groups and layers of hydrated water.

Precipitated Silica Process

The precipitation process is capable of the largest ranges of product properties. Particle size is determined through reaction conditions and mechanical reduction. Typical particle sizes are between 1 - 12 µm. There is also a broad range of macro pore volume attainable. Oil absorption values between 70 - 300 cc/100g are available. Surface areas tend to be less than gels with 60 - 250 m^2/g B.E.T., typical. The recent development of hybrid silica pigments have extended the range of specific surface area up to 600 m^2/g B.E.T.

Precipitated silica pigments are the result of the same polymerization that creates the silica gel networks. The conditions are controlled to produce discreet silica particles that covalently bond to one another to produce clusters or agglomerated particles. Control of the process gives rise to varied levels of internal porosity. The pores are tightly distributed and can be located at various size regions.

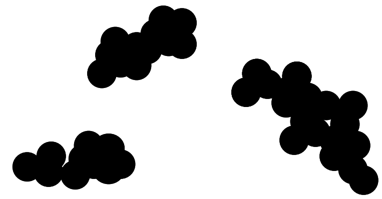

Figure 3. Illustration of precipitated silica agglomerate particles

Precipitated silica pigments like gels have surfaces covered with reactive silanol groups and layers of water of hydration as shown in Figure 4, below.

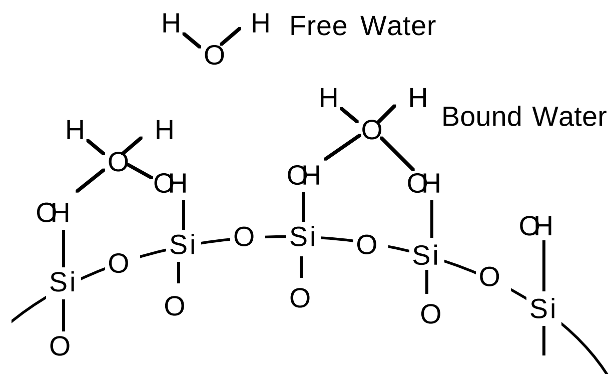

Figure 4. Synthetic silica surface showing associated water

The pigment industry has used simple and quick tests such as the rub out oil absorption method[5] to compare the relative functionality of products. While methods like oil absorption or water pore volume are useful they lack the sophistication demanded by today's applications. Producers of pigments understand that the porosity characteristics of the silica pigment are a key factor in differentiating products and relating their performance.

Porosimetry Measurement

There are a number of ways to determine a particulate's pore volume with lesser and greater degrees of accuracy. Oil absorption and water absorption are crude, but useful methods. These methods give an indication of volume but say little or nothing about pore size distribution. One method widely used by industry to assess the porosity characteristics of various materials is mercury porosimetry. In this method, mean pore radius, r, is related to minimum applied pressure, p, required to push a known liquid into a cylindrical pore, according to the Washburn equation:[6]

$$2r = -4\,\gamma(\cos\theta/p \quad (1)$$

where γ is the surface tension of the liquid and θ is the contact angle of the liquid (θ= 140º, γ= 480 dyne/cm at 293ºK for mercury).

Extensive data is generated in a typical porosimetry measurement routine. The data is presented as the distribution of pore volume across a range of pore sizes from 1000 down to 0.001µm, diameter. The data is manipulated to provide a distribution of cumulative, differential and log differential volume information. The technique is particularly useful in the evaluation of porous powders, although it breaks down rapidly below pore diameters of 0.005µm. The pressures required to force mercury into smaller and smaller pores becomes unattainable in commercially available instruments. To study the microporosity it is necessary to supplement mercury methods with a sophisticated multipoint nitrogen surface area methodology which will provide data down to 10µm or less. In using mercury porosimetry we have found differential volume versus pore size as well as total cumulative pore volume, $V_{p(Hg)}$, to be the most useful data and will rely on discussion of that data as the basis of this work.

Differential intrusion volume is the first derivative of the cumulative pore volume as a function of the calculated log diameter. This is normalized by the diameter interval, evenly dividing the range of the data acquired. Cumulative volume measurements are interpolated versus the log diameter to get the specific intruded volume, Vp_i, for the i^{th} point corresponding to evenly spaced log diameters. The data is subjected to a first derivative calculation, using nine-point smoothing. This allows the differential volume to be expressed in terms of uniform intervals of collected data.[7]

$$\textit{Differential Vol, } dVp_i = -Vp_i / D_i - D_{i-1}: \quad (2)$$

where, D is the calculated pore diameter for the *ith* point.

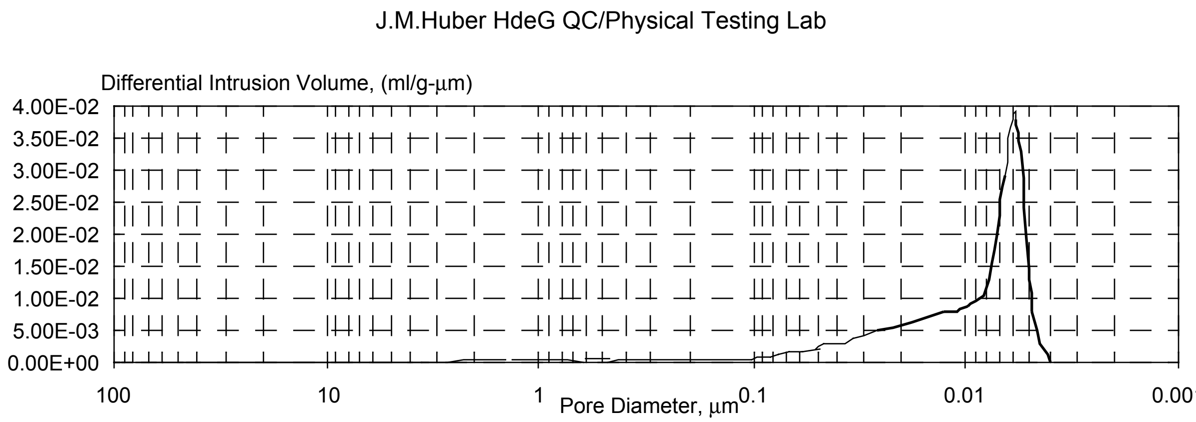

Figure 5. Comparison of Typical Pore Distribution

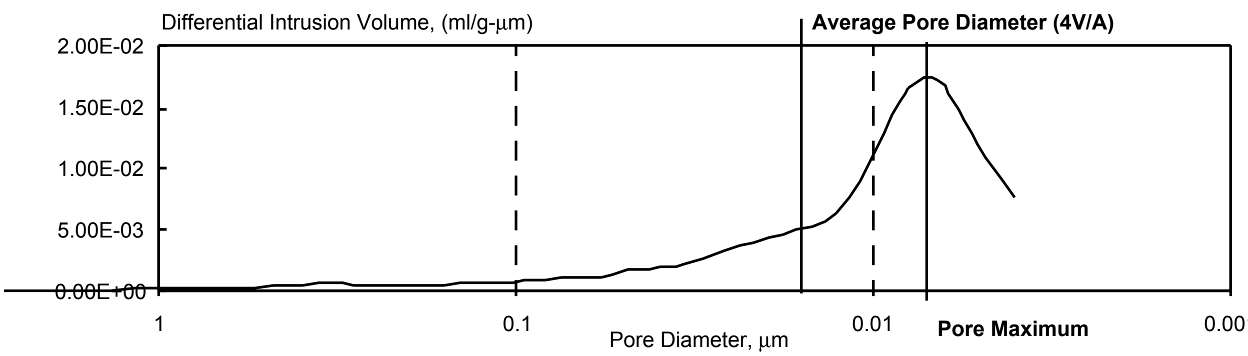

Figure 6. Illustration of Average Pore Diameter and Pore Maximum.

High structure synthetic silica pigments have a distribution of pores ranging in size from 100 down to 0.001µm. Although there is significant pore volume measured between particles, in the macro pore range (above 0.05µm diameter), a majority of pores are usually distributed around one specific size. Around this pore maximum, pores are normally distributed. The median pore size for commercially available silica pigments is generally between 0.05 and 0.005µm, in the range referred to as meso pores.[8] The location of the maximum within this range will be compared to the average pore diameter for each of the samples evaluated in this work.

Table 1. Series of Synthetic Silicas, Type and Key Physical Characteristics.

Silica Class (Process)	Average Particle Size[9], µm	Surface Area, B.E.T., m^2/g	Pore Volume ccHg/g	Average Pore, diameter, µm	Pore Maximum, diameter, µm
Precipitated	6.2	626	3.36	0.0422	0.0048
Precipitated	14.0	183	5.10	0.1000	0.0360
Hybrid	7.3	269	4.06	0.0396	0.0462
Hybrid	3.8	343	5.39	0.0608	0.0466
Hybrid	4.0	164	7.28	0.1502	0.0432
Gel	4.9	350	4.79	0.0636	0.0100
Gel	10.4	245	2.78	0.0266	0.0084
Gel	9.4	402	4.49	0.0328	0.0030
Fumed	22.0	206	13.07	0.2078	0.0240
Fumed	29.3	356	11.85	0.1482	0.0418
Fumed	36.1	166	7.76	0.1300	0.0484
Fumed	27.3	201	13.25	0.1850	0.0550

Selection of Silica Pigment Samples

To study the impact of porosity we chose several silica pigments with differing pore size distributions. We selected samples within a specific silica manufacturing technology and across technologies to provide a series. Silicas with pore maximums between 0.05 µm diameter and 0.005 µm diameter were included.

We were able to secure a series of samples that adequately covered the range needed. The set of samples consisting of the precipitated/hybrid and gel silicas cover a range from 0.003 to 0.05µm, with pore maximums evenly distributed. The series of fumed products cover a narrower range extending from 0.025 to 0.045 µm at the higher side of the overall range of pore maximums.

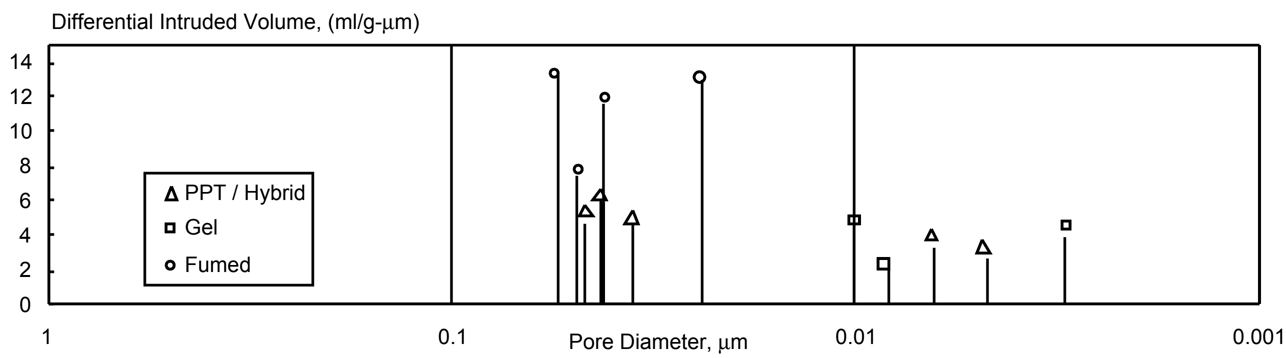

Figure 7. Range of pore maximum cove red by samples evaluated in this series.

Preparation of Sample Papers

Sheets of a common basestock were coated using a Dow Bench Blade Coater to nominal coat weight of 3 g/m^2 (c1s). The coating color was kept simple with a 1:1 pigment binder ratio, silica to polyvinyl alcohol. A partially hydrolyzed vinyl alcohol was utilized. Coating solids ranged from 16% to 21.3%, while achieving equal coat weight was the criteria. Sheets were coated, lightly calendered, die cut to $8^1/_2 \times$ 11″ and equilibrated under standard TAPPI conditions for 24 hours before being tested.

There have been a variety of techniques developed to quantify differences in ink jet printability. The majority of these tests attempt to describe differences in the shape and size of the printed dots generated by a specific printer. We wanted to choose a well known test pattern that provided a large array of dots and wanted solid color areas for color density measurements. We chose an HP Deskjet[10] 500C series printer and utilized software provided by Hewlett-Packard.[11] We realize that more modern printer architectures are capable of better print resolution, but we felt the 500C still would be representative of a significant portion of the installed base of ink jet printers. Using an image analysis system consisting of a Nikon microscope, CCD video camera and PC based software, we measured the average dot area of the composite black dots. We also evaluated the roundness of the dots. Roundness is determined by calculating the perimeter of a perfect circle having an area matching the measured pixel area. The perimeter of that ideal circle is compared to the measured perimeter to arrive at a roundness value. A bench type reflectance densitometer with a 3mm window was used to make measurements of color density on the solid printed areas of the test pattern used.

Relating Pore Distribution to Key Ink Jet Print Properties

Dot Area

Single printed sheets representing each silica containing coating were evaluated. Measurements were taken on a printed array of 38 × 39 dots. Samples were taken at four positions within each array for each of the coated sheets. In the analysis all boundary particles were discarded and area was measured on individual dots. The array was sampled by taking images in four regions, UL, M1, M2 and LR. The mean area from each sheet's distribution was compared to the respective key physical characteristics of each silica in a simple correlation matrix.

Dot Roundness

The same array sampling procedure was used when evaluating the effects on dot roundness. In the case of roundness the average roundness of each position (38 - 42 dots) was averaged to yield a roundness for the sheet. Analysis of the composite black dots and analysis of cyan dots was completed.

Color Density

In previous work we have observed that coating formulation, will impact the individual ink jet process colors differently. Rather than attempt to deal with effects on each individual color, we have chosen to look at a composite color index as being representative of the overall color density of the sheet. This is simply,

$$\text{Composite Color density} = OD_{cyan} + OD_{yellow} + OD_{magenta};$$

where OD is the optical density of the solid area of the particular process color.

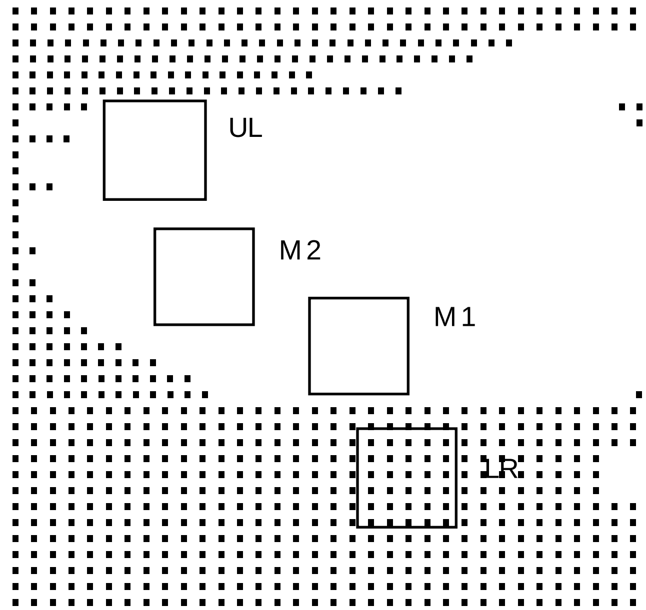

Figure 7. Representation of four positions in dot array sampling.

The sum of the individual densities. Density measurements were made on sheets 24 hours after printing. A total of five readings were taken with an X-Rite 418 Densitometer, and averaged to yield the result.

Correlation of Results

Data was placed into a spreadsheet and a simple correlation matrix produced to look at first order influences. Surprisingly, some very strong influences were observed.

Table 2. First Order Correlation Matrix, r^2. Complete data set.

	Dot Area	Dot Roundness	Composite Color Density
Average Pore Size, µm	-0.85	0.75	-0.74
Pore Maximum, µm	-0.61	0.58	-0.65
Total Pore Volume, ccHg/g	-0.84	0.52	-0.68
Oil Absorption, cc/100g	-0.26	0.41	0.05
Average Particle Size, µm	-0.82	0.21	-0.72
Surface Area, BET, m^2/g	0.51	-0.61	0.37

Correlation with Dot Area

Some interesting observations can be made when looking at the relationships between product properties and corresponding print properties. We were surprised with the strong correlation observed with Dot Area measurements. Pore size and volume showed a very strong relationship with area as did silica average particle size. Particle size adds porosity on a macro scale through disruption or "structuring" of the coating. Smaller sized particles, typically having more per unit volume, will more evenly disrupt the coating and allow more dot spread into the pores of the coating or silica. Correspondingly, larger pore sizes offer easier access and allow the ink to spread and dot area to increase.

Average Pore Size

Average pore size is determined for this study based on the assumption that all pores are cylindrical, using the relationship (4 Pore Volume/Area). This is a standard assumption used by most commercial porosimetry routines. We observed that average pore size related well with dot area, dot roundness and color measurements. Although this was not the basis used in the selection of silica pigments, it is surprising knowing the differences between fumed and the other classes of silica pigments that this proved to have a strong impact on all the print properties measured. Even despite their differences, the group of fumed silicas fell cleanly within the entire dataset. This is particularly the case in dot roundness in which the group of fumed silicas showed that increased average pore diameter contributed to improved roundness. By splitting the overall dataset into classes we can see that the behavior within each class is very similar with correlation highest for the group of gel silicas.

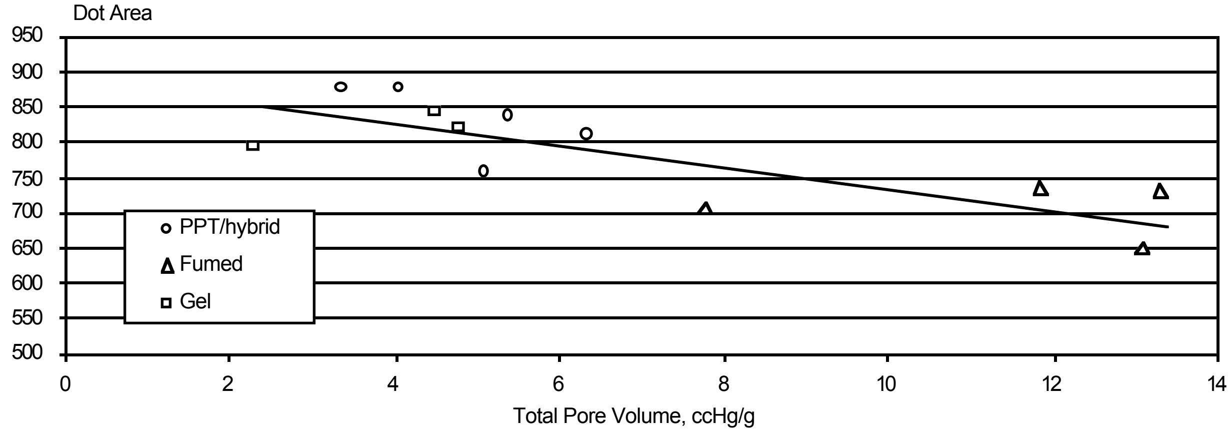

Figure 8. Relationship between dot area and total pore volume. $r^2 = -0.85$.

Correlation with Dot Roundness

Very good correlation between dot roundness and silica pore structure was observed. The relationship of total pore volume and roundness had the lowest correlation of the entire data set. This can be attributed to the lack of correlation within the fumed and gel data sets. The precipitated/hybrid data was highly correlated with higher total pore volume yielding better dot roundness as shown in Figure 9.

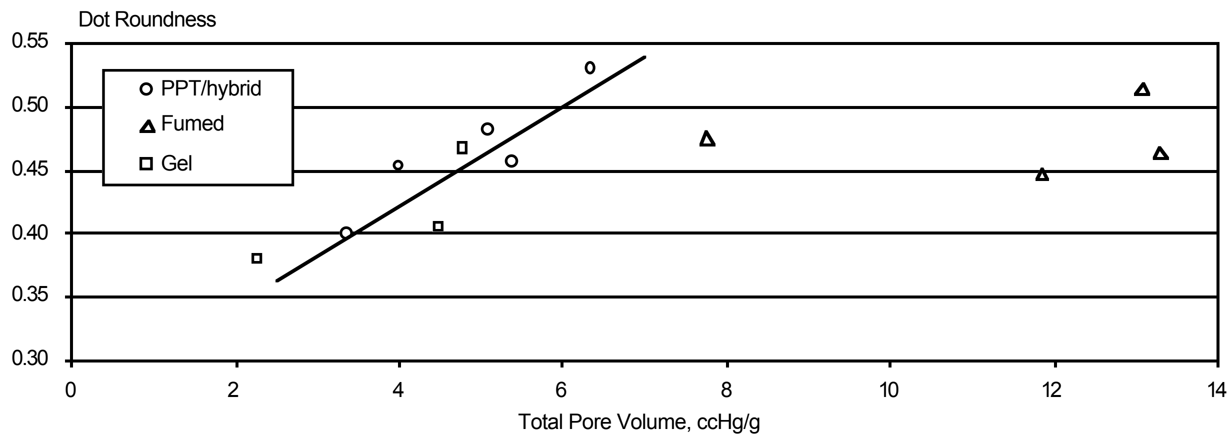

Figure 9. Strong correlation with precipitated / hybrid silica pigments and dot roundness. $r^2=0.94$.

There was strong correlation with average pore volume and slightly poorer correlation with pore maximum. Average pore size showed a strong relationship across the entire data set. The series of gel silica pigments appear to have shifted slightly to lower roundness values.

Correlation to Composite Color Density

The best correlation with the composite color density was observed with the pore maximum. The slope of the resulting relationship was quite low showing only a 10 percent effect over the range of the data set. It is noteworthy that similar strong correlation is observed between pore properties and dot area. The interrelationship between dot area and color is well known with larger dots completely filling the solid printed area leaving no exposed unprinted base to lower overall print density. In this study that relationship was not clear ($r^2 = 0.46$); however, the impact of changes in dot area was substantial. A change in dot area of 100 yielded the same 10% change in composite color observed over the entire range of the data set.

Of interest is the impact of the silicas by class on the color properties of the print. If we simply sort the data set by composite color and observe the relative rank of each silica type, you can clearly see that the precipitated/hybrid silicas are at the top along with the silica gel pigments, yet the fumed products tend to be ranked at the bottom. As all the coatings were simple two component systems and coat weights held very close we can presume that this can be attributed to the silica pigment. In the discussion at the beginning of the paper you will remember that the gel and precipitated products are produced in an aqueous system and have a highly hydrated surface, while the fumed process yields unhydrated glassy particles. Although all three types have surfaces populated with silanol groups, the hydration of the surface seems to yield a benefit in the interaction of the ink dyes and the silica pigment.

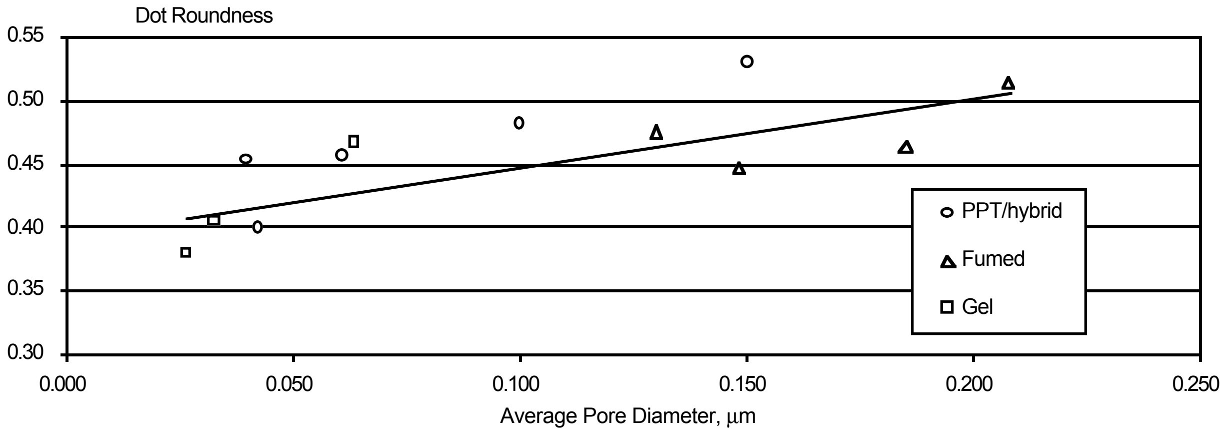

Figure 10. Relationship between silica average pore diameter and dot roundness. $r^2 = 0.74$.

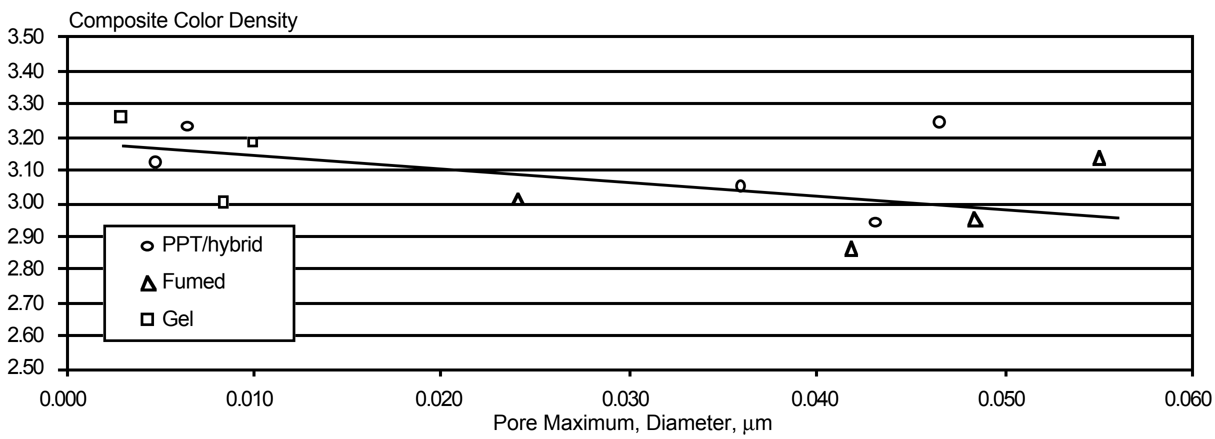

Figure 11. Influence of silica pore maximum on print color density.

Conclusions on the Importance of Silica Pore Structure

Total Pore Volume

Not surprisingly total pore volume correlated well with all the ink jet properties we studied. The portion of the pore volume below 0.1µm correlated better than the pore volume above 0.1µm. This is a clear indication of the importance of the internal as opposed to the external or intraparticle pore volume. The strongest impact of total pore volume was on dot area, with increases in pore volume decreasing dot size as the added porosity arrested the ink spread through the coating. Previous work looking at the degree of z-directional penetration into a coated sheet showed the ability of a silica containing coating to arrest penetration of the ink at the surface of the sheet.[12] Impact on dot color was also strongly correlated. The relationship between dot area and color, as discussed previously, contribute to this.

Table 3. Rank of Silica Class and Composite Color Density.

Silica Class	Composite Color	Ranking
Gel	3.26	*Best*
Hybrid	3.24	″
Hybrid	3.23	″
Gel	3.18	″
Precipitated	3.12	″
Precipitated	3.05	″
Fumed	3.01	*Intermediate*
Gel	3.00	″
Fumed	2.98	″
Fumed	2.95	″
Hybrid	2.94	″
Fumed	2.90	″
Fumed	2.86	*Poorest*

Average Pore Size

Average pore size is determined for this study based on the assumption that all pores are cylindrical, using the relationship (4 Pore Volume/Area). This is a standard assumption used by most commercial porosimetry routines. We observed that average pore size related well with dot area, dot roundness and color measurements. Although this was not the basis used in the selection of silica pigments, it is surprising knowing the differences between fumed and the other classes of silica pigments that this proved to have a strong impact on all the print properties measured. Even despite their differences, the group of fumed silicas fell cleanly within the entire dataset. This is particularly the case in dot roundness in which the group of fumed silicas showed that increased average pore diameter contributed to improved roundness. By splitting the overall dataset into classes we can see that the behavior within each class is very similar with correlation highest for the group of gel silicas.

Color density also correlated well with average pore size. Smaller pore sizes yielding improvements in color.

Table 4. Correlation of Macro and Meso Pore Volume Influences, r^2.

	Dot Area	Dot Roundness	Composite Color Density
Total Pore Volume, $Vp_{(Hg)}$,ccHg/g	-0.84	0.52	-0.68
Pore Volume, > 0.1µm diameter	-0.48	0.29	-0.02
Pore Volume, > 0.1 to 0.01µm diameter	-0.85	0.54	-0.71
Pore Volume, < 0.01µm diameter	-0.57	-0.72	0.58

Table 5. Correlation of Individual Silica Classes with Average Pore Diameter (4 Vol/Area) Verses Dot Roundness.

Class	Correlation Coefficient, r^2
Precipitated / Hybrid	0.90
Gel	0.99
Fumed	0.68
Complete Silica Dataset	0.75

Pore Maximum

The pore maximum used as the selection criteria in this work, showed good correlation with the measured properties. Of interest is the fact that the pore maximum was in most cases negatively correlated when average pore size was positively correlated, and vise versa. In each case strong correlation was achieved. It is obvious upon closer examination that this is an artifact of the small number of data points in the determination. In Table 6, data that is believed to be in error is signified by the addition of an astrisk (*).

We were surprised that the pore maximum property was of less practical use than the average pore size. Within each class there were some correlations, but overall average pore diameter appears to be the more powerful descriptor for a synthetic silica pigment.

Table 6. Correlation of Ink jet Printability with Average Pore Size and Pore Maximum.

FUMED	Dot Area	Dot Roundness	Composite Color Density
Average Pore Size, µm	-0.73	0.68	0.52*
Pore Maximum, µm	0.65*	-0.68*	-0.67
GEL			
Average Pore Size, µm	0.19*	0.99	0.37*
Pore Maximum, µm	-0.71	0.44	-0.57
PPT / HYBRID			
Average Pore Size, µm	-0.70	0.90	-0.88
Pore Maximum, µm	-0.69	0.71	-0.34

Combined Effect Model

To better visualize the interplay of the impact of pore volume and average pore size, the data was modeled using a statistical software package. The limited data was subjected to a Kriging[13] algorithm to fill any missing data points in the model and smooth the data. This method allows the known or measured data to be preserved increasing the validity of the model that is produced. Comparison of the combined effect of Pore Volume and Average Pore Diameter on color density showed pore volume to be the significant and controlling variable. It is interesting that the maximum roundness is achieved at pore volumes from 3.5 to 5.5 ccHg/g as determined by mercury porosimetry. Increased pore volume beyond 6 ccHg/g yields a significant drop in color density. This drop can be directly attributed to the samples of fumed silica. Recall that these materials had very high volumes of meso porosity which in our model does not benefit color development. Samples at the maximum range of color development are the gels and the hybrid precipitated pigments.

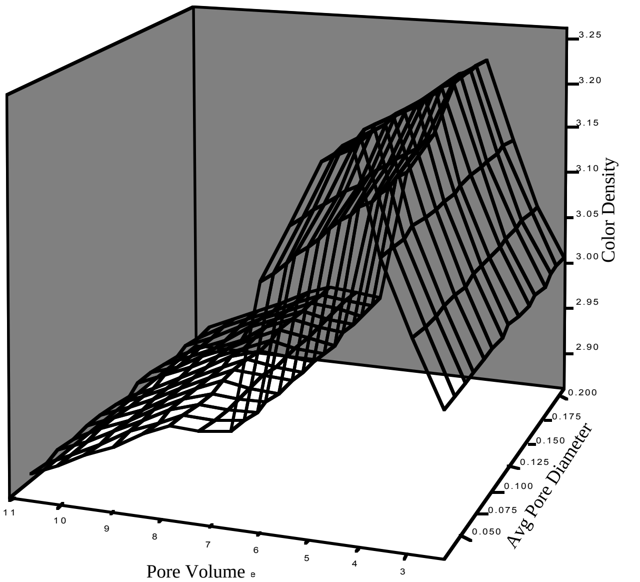

Figure 12. Surface Model of Porosity Effects on Composite Color Density.

As was observed above, the total Pore Volume appears to be the significant variable controlling dot roundness. The impact of Average Pore Diameter is perceptible, but slight. In this case we observe that, once again a roundness maximum is indicated. The maximum occurs at a Pore Volume between 6 and 8 ccHg/g and remains strong through 11 ccHg/g, the area dominated by fumed silica pigments.

Final Remarks

Porosimetry measurement is a powerful technique. It is clear from this and other work that the assessment of pore properties of a pigment should be an important criteria when comparing candidates for ink jet coatings. The strong correlation of simple print properties show the need to have a detailed understanding of both silica pore distribution and silica class. More extensive study will be necessary to understand in detail the differences in the behavior of the liquid process silica pigments and the fumed products, before a complete picture of the interaction of these pigments in the complex ink jet coatings can be understood.

Acknowledgments

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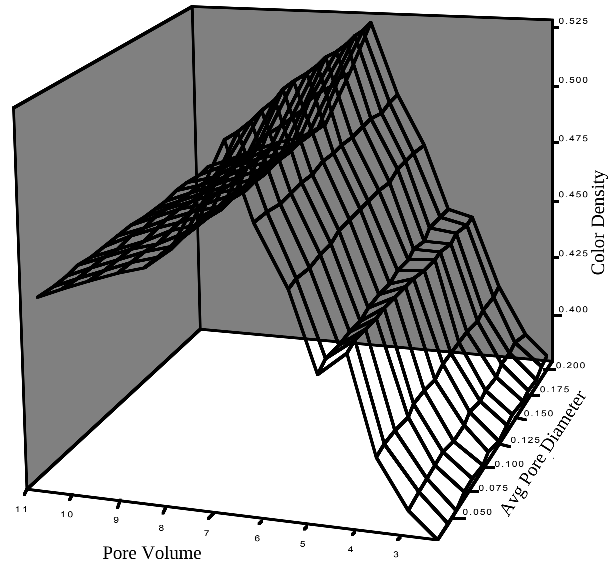

Figure 13.

References

1. Iler, R. K., "The Colloidal Chemistry of Silica and Silicates", Cornell University Press, Ithaca, NY, 1955, p. 3. 1955, p3.
2. Jell-O is a registered trademark of General Foods Corp.
3. L. Kutik, "Structure and Properties of Amorphous Silica Gel in Coating Applications", Presented 63rd Annual Meeting of Federation of Societies for Coatings Technology, October 9, 1985, St. Louis, MO.
4. K. Unger, Porous Silica, Its properties and use as support in column liquid chromatography, *Journal of Chromatography Library*, **16**, p. 47, 1979.
5. ASTM Oil Absorption of Pigments by Spatula Rub-out, D 281 - 31. (Re-approved 1980).
6. Washburn, E. W., *Proc. Nat. Acad. Sci. US*, "Note on a Method for Determining the Distribution of Pore Sizes in a Porous Material," **7**: 115 (1921).
7. Micrometics AutoPore II 9220 Operators Manual, V 3.03, Appendic D, 2-3, January 1994.
8. IUPAC, Manual of Symbols and Terminology, Appendix 2, Part I, Colloid and Surface Chemistry, *Pure Appl. Chem*., **31** (1972) 578.
9. Particle size determined using a Leeds and Northrup Microtrac II laser light scattering instrument.
10. HP and DeskJet are registered trademarks of the Hewlett Packard Company.
11. *Hewlett Packard Paper Acceptance Criteria for the HP Deskjet 500C*, First Edition, 11-30-92.
12. Withiam, M.C., et al., "Precipitated Silica Pigments for Color Ink jet Improvement", 1994 *TAPPI Papermakers Conference Poster Session*, April 23-24, Chicago, Il.
13. Fortner, B., The Data Handbook, Version 1.0, Spyglass, Inc. Champaign, Il (1992).