High Performance Porous Inkjet Media Derived from Fumed Silica

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Abstract

Fumed silica is the most important inorganic oxides used for the high performance porous inkjet media due to its high ink absorbing capability, hydrophilicity, and ease of modification. To improve the water fastness of the anionic dye, the surface of the fumed silica need to be modified from negative charged to positive charged. In this paper, different methods to convert the surface charge of fumed silica, and their advantages and disadvantages will be discussed. The chemicals used to treat fumed silica include aluminum chlorohydrate(ACH), aminosilanes, mixture of ACH and aminosilanes, and addition of cationic polymers. A novel process has been developed to treat fumed silica with silane coupling agent in water and their advantages will be discussed. The image quality, the stacking permanence, the durability, and the water fastness of the porous inkjet media comprising these fumed silicas will be compared and discussed.

Introduction

Inkjet printing technology has become the dominant printing method for commercial large format and desktop small format printing for photo, graphic art, and document. Advantages of the inkjet printing includes print on demand, high color gamut, high image quality, and ease of use. For photo printing, there are two major types of inkjet media in the market: swellable or polymeric, and porous. Swellable inkjet media has coating of water soluble polymers as binder, cationic polymer (so-called mordant) to fix the dye, the crosslinker to improve water resistance. Examples of polymer include polyvinylalcohol(PVOH), polyvinylpyrolidone (PVP), gelatin, copolymer of PVOH and PVP, or mixtures above. Examples of the cationic polymers include Polydiallyldimethylammonium chloride (DADMAC), acrylic polymers and styrene acrylic polymers containing primary, secondary, tertiary and quaternary amines, polyethyleneimine (PEI), guanidine and bigualidine, and salts of Al and Zirconium. Porous inkjet media comprising inorganic oxides such as fumed silica, boehmite, fumed alumina, colloidal silica, polymer binders such as PVOH and gelatin, and cationic polymers.

Advantages of the swellable media are better light and ozone fade resistance, better manufacturability but disadvantages are long drying time, poor finger print resistance, poor pigment ink performane and poor water resistance, On the other hand, porous inkjet media is better in drying time and water resistance but suffering from poor ozone fade resistance. In recent years, porous inkjet media has become the favored media because of better gloss, fast drying time, better handling, and better IQ for pigmented ink.

Fumed silica is the most important inorganic oxides used for the porous media because of its high ink absorbing capacity and transparency. The surface of fumed silica is negative charged at pH 2 and above so the affinity to the negatively charged dye is poor. There are several methods to modify the surface of fumed silica so the net surface charge is positive at pH 4-5. In other words, the isoelectric point (IEP) of the fumed silica need to be at least 6 and above.

The most common and conventional method is to react fumed silica with aluminum chlorohydrate (ACH)[1]. ACH is the base hydrolysis product of aluminum chloride and is used widely for water treatment. Depending on pH, ACH is mixture of polynuclear species and the most common species exit at pH 4 is Al_{13} ions. The existence of Al_{13} ions has been confirmed by X-ray and ^{27}Al NMR (63.5 ppm) which attributed to the single tetrahedrally coordinated aluminum located at the center of three layers of edge-sharing octahedral[2]. Second method is to react fumed silica with silane coupling agent containing amino functional group. Most common example is 2-aminoethyl-3-aminopropyltriethoxysilane. This usually carried out in organic solvents such as methanol but we have developed a process to react fumed silica with aminosilanes in aqueous solution in good yield. Third method is to react fumed silica with the combination of ACH with aminosilanes in aqueous solution. Fourth method is to contact fumed silica with cationic polymers, such as poly(DADMAC). In this case, cationic polymers are adsorbed strongly on the surface of fumed silica and cause charge reversal.

Experimental

Cabot Cab-O-Sil M-5 and MS-55 fumed silica were used in this study. Kady Lab model rotor/stator was used for the dispersion of fumed silica. Malvern Zetasizer was used to measure the Z-ave particle size and the isoelectric point of the modified fumed silica. The cationic fumed silica prepared by different methods are converted at different condition to ensure the conversion is complete and yields is high. The coating formulation comprising cationic fumed silica, binder, surfactant, crosslinker, and plasticizer are mixed in a lab mixer. The coating on gel-subbed photo paper was by either hand drawdown or on a pilot coater.

Silica Treatment

Fumed Silica Treated with Aluminum Chlorohydrate (ACH) (Type I)

The reaction of fumed silica with ACH is very straightforward but a lot of energy is required to disperse the silica. The viscosity of the silica dispersion tends to get very high and aggregate of the fumed silica is difficult to break completely. In addition, fairly large quantity of ACH is required to convert the surface silanol group to the aluminum oxide. The porous inkjet formulation comprising ACH fumed silica tends to have very high viscosity and high coating defects. The coating tends to be hazy and has poor image quality (low gamut and black density). Fig.1 showed the structure of ACH and the change of IEP with level of ACH treatment.

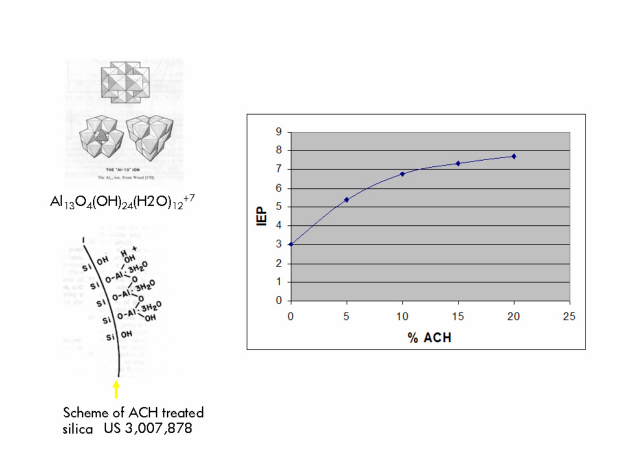


Fig.1. IEP of ACH Treated Fumed Silica

Fumed Silica Treated with Amine Silane Coupling Agent (Type II)

Amino functional group can be introduced on the surface of inorganic oxides with the amino silane coupling agents (Fig. 2). Most common amino silane coupling agents are listed in Table 2. Traditionally, the treatment of inorganic oxide with silane coupling agents is carried out in organic solvent at reflux temperature with trace amount of water3. However, this procedure is tedious, expensive, and the dispersion quality is poor for inkjet application. We have developed a improved procedure such that fumed silica dispersion can be treated with amino silane coupling agents in aqueous solution with excellent yields. For comparison purpose, we treated Cab-O-Sil MS-55 with 3-aminopropyltrimethoxy silane in MEK and in water (Fig.3).

It is clear that aqueous process have the advantages of better process, higher yields, less side reaction, better dispersion and coating quality. The reaction of amino silanes with fumed silica in water is confirmed by solid state Si29 NMR (Fig. 4). The relationship of the isoelectric point (IEP) with level of amino silanes is almost linear and this further confirm the reaction is almost quantitative (Fig.5). However, Type II silica tend to have poorer water fastness and humid fastness than the Type I silica.

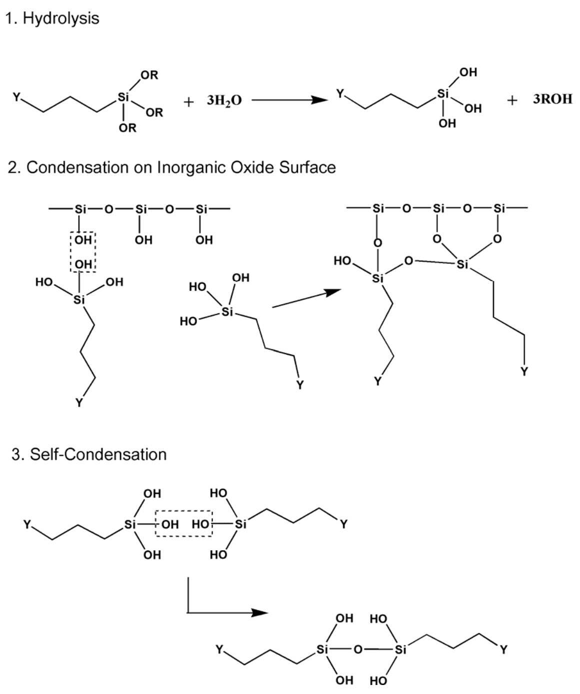


Fig.2. Reaction Scheme of Silane Coupling Agents with Silica

	MEK Process	Aqueous Process
Process	Multiple steps	One step
Yields	Low	High
Isoelectric Point	8.36	8.91
Z-Ave Size (nm)	180nm	125nm
Color	Deep purpled	Colorless
Dispersion and Coating	Bad	Good

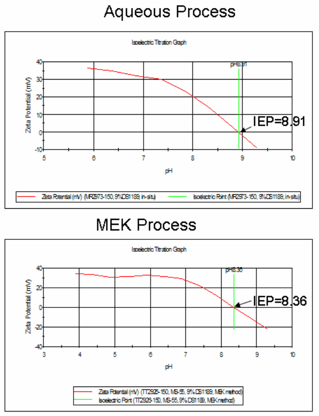


Fig. 3. Comparison of Silane Coupling Reaction in MEK and in Water

% ACH	% Silane	IEP
3	8.46% Silane b	8.43
3	6.86% Silane c	8.46
3	7.39% Silane d	8.5
3	5.25% Silane e	8.52
3	8.45% Silane f	8.62
3	8.45% Silane g	8.71
3	8.46% Silane h	8.95
3	9.00% Silane a	9

Table 2. Most Common Amino Silane Coupling Agents.

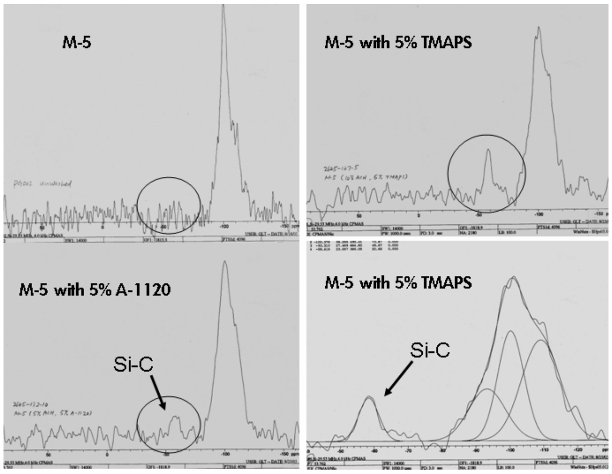


Fig. 4. ^{29}Si NMR of Cab-O-Sil M-5 Treated with 3-aminopropyl trimethoxysilane in water

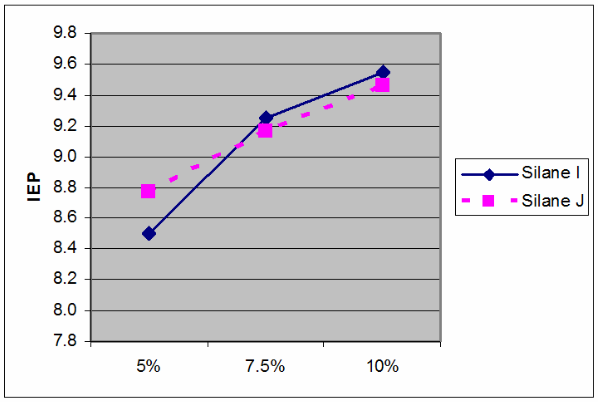


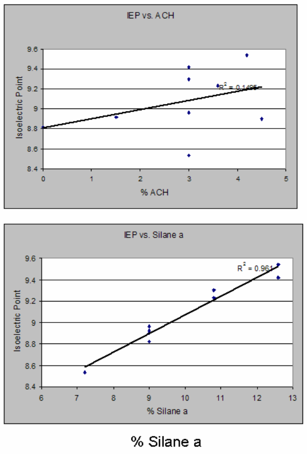
Fig. 5. Isoelectric Point (IEP) of Cab-O-Sil MS-55 Treated with 5%, 7.5% and 10% of Silane I and J in Water.

Fumed Silica Treated with ACH and Amino Silanes (Type III)

In this process, ACH and amino silanes were reacted first followed by the addition of fumed silica. The advantages of this method are the ease of dispersion and the best overall coating and photographic performance. It was discovered that IEP is much more sensitive on the level of amino silanes and is independent to the level of ACH (Fig. 6). However, not all amino silanes have same performance at equal molar basis(Table 3). Alkylated aminosilane tends to have higher IEP than the unsubstituted amines.

Addition of Mordant Polymers (Type IV)

This probably the easiest way to convert fumed silica. IEP increase proportionally to the level of the mordant polymers (Fig.7). However, the coating mix tends to have very high viscosity indicating that mordant polymers are only adsorbed on the surface. The addition of binder, e.g. PVOH, deplete mordant polymers from the silica surface and interact strongly with the silica surface. This indicate that IEP is not a reliable tool to monitor the conversion of silica treatment.



ACH	Silane a	IEP
3	7.2	8.53
0	9	8.82
1.5	9	8.92
3	9	8.96
4.5	9	8.9
3	10.8	9.3
3.6	10.8	9.23
3	12.6	9.42
4.2	12.6	9.54

Conclusion:

Isoelectric point is dominated by the level of the aminosilanes and is insensitive to ACH level.

Fig. 6. Relationship of IEP with ACH and Amino Silanes

% ACH	% Silane	IEP
3	8.46% Silane b	8.43
3	6.86% Silane c	8.46
3	7.39% Silane d	8.5
3	5.25% Silane e	8.52
3	8.45% Silane f	8.62
3	8.45% Silane g	8.71
3	8.46% Silane h	8.95
3	9.00% Silane a	9

Table 3. IEP Comparison of Different Amino Silanes at Same Treatment Level

Coating and Photographic Evaluations

Comparison of Type I, II and III Silicas

Typical coating formulation for the porous inkjet media is shown in Table 4. Comparison of the coatings and photographic performance derived from three types of cationic fumed silica are shown in Table 5. For coating quality, *Type I* silica tends to be the worst and *Type II* is the best. For image quality, *Type I* tends to be the worst and *Type II* is the best again. For dispersion and process, *Type II* is the best. *Type I* treatment generally need large amount of ACH in order to reach the desired isoelectric value. The dispersion is not as stable as the other two types and their coatings have high viscosity and coating defects. The image quality of *Type I* dispersion is also the worst because the coating is much hazier than other two dispersions. *Type II* dispersion is the best in image quality and stacking performance but durability and water fastness is not good. *Type III* dispersion has the best overall performance in dispersion, coating, image quality, stacking performance, and water fastness.

Table 4. Typical Porous Inkjet Coating Formulation

	Parts
Cationic Fumed Silica	100
Polyvinyl Alcohol	15-22
Boric Acid	1.5 to 3.0
Plasticizers	0.5 to 1.5
Additives	0.5 to 1.5
Surfactants	0.05

Table 5. Comparison of Three Cationic Fumed Silic

Treatment	ACH only	ACH and Silanes	Silanes only
Manufacture	– – –	++	+
Image Quality	– –	+	++
Stacking Haze	– –	+	++
Stacking Colorshift	– –	+	++
Stacking bleed	+	+	–
Humid Fastness	+	+	–
Water Fastness	+	+	–
Light Fastness	++	+	–
Ozone Fastnes	++	+	–

Effect of Treatment Level

In comparison to the traditional AgX print, one of the major disadvantages of the dye based inkjet photo is the poor waterfastness. One of the questions is what happen if we keep increasing IEP and treatment level. In this study, we investigated the effect of treatment level on IEP, waterfastness, image quality and stacking performance. As expected, IEP increase linearly with % silanes (Fig.5) so as the waterfastness and stacking bleed (Fig. 7 and 9). However, increasing % treatment has adverse effect on image quality (gamut, L*min), stacking colorshift, and stacking haze(Fig.8, 9).

Conclusions

Combination of ACH and amino silanes is the best way to convert negatively charged fumed silica to the cationic fumed silica and the inkjet media comprising this silica has best overall performance. Not all amino silanes have same performance at equal molar basis. Increasing treatment level only improve waterfastness and bleed, but image quality and other stacking performance get worse.

References

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Author Biography

Tienteh(TT) Chen received his BS in Chemistry from the National Taiwan University in 1974, MS in Organic Chemistry from the University of Illinois in 1979, and PhD in Polymer and Colloids Chemistry from the University of Connecticut in 1983. He joined the Polymer Science and Technology Lab of the Eastman Kodak Company in 1986 and worked in the area of AgX and Digital Printing Technology. He was nominated to the Gallery of Outstanding Inventors in 1999. He joined the Inkjet Media R&D Division of the Hewlett Packard Company in 2001. He is (co)author of 42 US patents in the area of AgX, Inkjet and Thermal Printing Technology.

Eric Burch received his B.A. degree in Chemistry from Grinnell College in Grinnell, IA in 1989 and a Ph.D. in Chemistry from Northwestern University in Evanston, IL in 1994. His academic work focused primarily on photochemical mechanisms in single molecules and polymeric systems. Starting in 1994 he held a post-doctoral position at Oak Ridge National Laboratories working on new materials development and fabrication. Since 1995, he has worked at Hewlett-Packard Company in San Diego, CA. He currently is a R&D Project Manager leading a team developing new media technologies for photo applications.

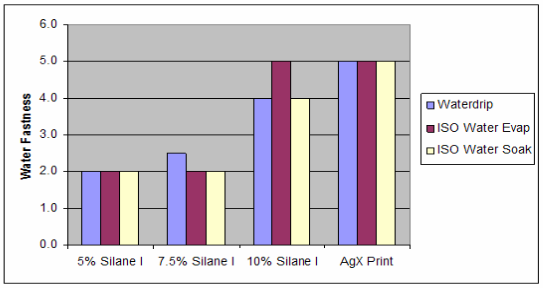
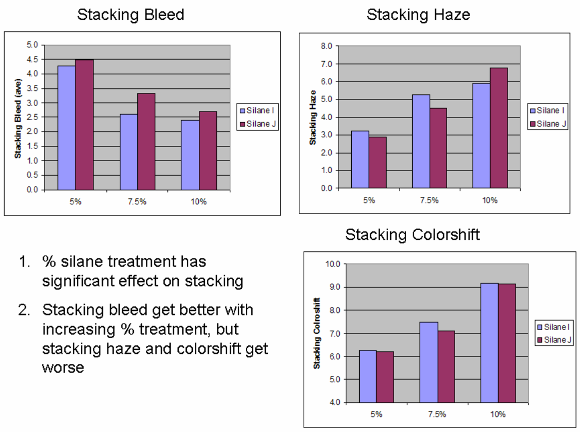


Fig. 7. Effect of % Treatment on Water Fastness



1. % silane treatment has significant effect on stacking
2. Stacking bleed get better with increasing % treatment, but stacking haze and colorshift get worse

Fig. 8. Effect of % Treatment on Image Quality