Sensient's S.M.A.R.T. 4000 Technology for Self-Dispersed, Polymer-Attached Nano Particle Dispersions for Inkjet Inks

Mihaela Madaras, P.K. Sujeeth, Dan Oullette, Mark Ulrich; Sensient Colors; St. Louis, MO/USA

Abstract

The methodology of attaching polymers on the surface of pigments using the S.M.A.R.T. (Surface Modification by Attachment via Radical disproportionation Technology) approach will be discussed. This method allows the "one-pot" attachment of polymers in addition to small molecules such as 4-amino benzoic acid. While the small molecules are attached through the intermediacy of 1,3,5-triazine derivatives, many polymers are amenable to incidental attachment in the presence of the free radicals generated in situ from 1,3,5-triazines species.

The benefits of attaching polymers to pigments include the overriding of the pigment-polymeric dispersant compatibility problems that sometimes occur and having greater flexibility in adjusting the pigment properties for inkjet printing.

Introduction

Today's digital printing market demands inks with high optical density, excellent chroma, great image durability and good jettability. All these attributes need to evolve at the same time with the printhead technology that advances towards faster printing and smaller drop size.

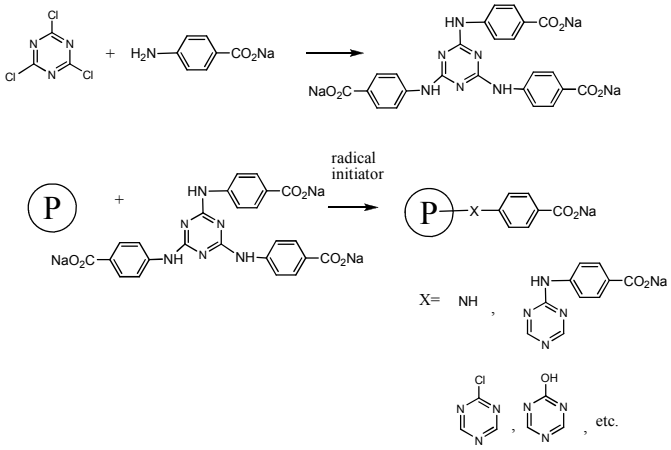
Self-dispersed pigments are usually known as a class of colorants that can deliver high OD and chroma with good jettability but are sometimes deficient in image durability (e.g. rub resistance, scratch resistance, highlighter smear).

Sensient's innovative approach to modifying the surface of nano-pigments is challenging the limitations of self-dispersed pigments addressing the needs of the printing industry by using a "tool-kit" approach. Our patent-pending technology to attach a wide variety of organic molecules, including polymers, allows great flexibility in producing pigments with desired properties. More specifically, our method can be customized to attach the molecules of choice in a highly efficient way.

Discussion

S.M.A.R.T. (Surface Modification by Attachment via Radical disproportionation Technology) chemistry developed by Sensient [1, 2] makes use of 1,3,5-triazine tris derivatives to generate radicals that can then attach to the surface of the pigment. The fragments that attach to the surface are negatively charged and thus create the electrostatic repulsion needed for stabilizing the particles in water. Scheme 1 shows the attachment reaction of a 4-aminobenzoic acid (4-ABA) tris derivative to a pigment particle. The synthesis of tris reagents is a simple process that occurs in water and starts with cyanuric chloride and the corresponding amino compounds (e.g. 4-ABA or other amines). Due to the stepwise nature of this substitution reaction, up to 3 different amines can be used to obtain mixed amino-1,3,5-triazines.

The resulting pigment dispersion family where the attached group on the surface is a small molecule is generically called S.M.A.R.T. 3000.



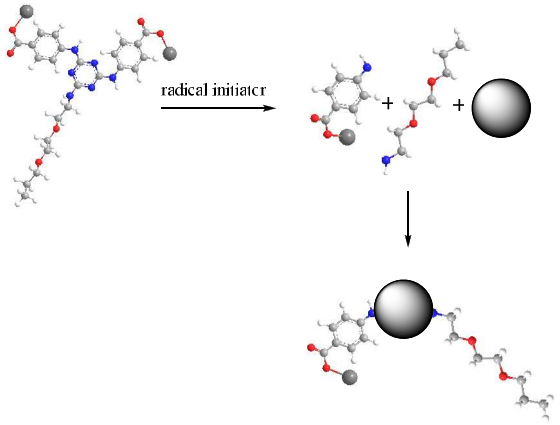
Scheme 1

Due to the high versatility of this chemical process, we expanded the technology to attach polymers to the pigment surface and create the S.M.A.R.T. 4000 line of pigment dispersions.

Usually, polymers are added to the inkjet inks to achieve image durability and media independence. However, frequently the polymer added to the ink ends up separating from the pigment on the paper offering no effect to the printed image. Attaching the polymer to the pigment ensures the close proximity of the two, obtaining the desired properties with the minimal amount of polymer.

The reaction described in Scheme 1 allows the attachment of polymers [3], either by pre-attaching a polymer to the 1,3,5-triazine ring (Protocol A, Scheme 2) or by incidental attachment, where a free-standing polymer able to form radicals has the potential to attach to the pigment surface during the reaction (Protocol B, Scheme 3).

Protocol A can use polymers that contain at least one amino group to be attached to the 1,3,5-triazine ring to obtain the radical-forming tris reagents. These tris reagents can contain one, two or three different substituents that can potentially attach to the surface. Examples of polymers include linear polyethoxy and polypropoxy polymeric amines with a known molecular weight range of 300-3000, available from Huntsman Chemicals under the trade name "Surfonamines" and polyethyleneimines (PEI) such as PEHA (pentaethylenehexamine) and Epomines. This protocol can be applied to raw pigments under milling conditions or to oxidized pigments such as Sensijet® Black SDP 100 and Sensijet® Black SDP 1000 self-dispersed pigments. All reaction mixtures are purified by ultrafiltration in order to remove salts and any unreacted tris molecules. This step renders a clean dispersion containing just the self-dispersed pigment in water without any extraneous impurities.

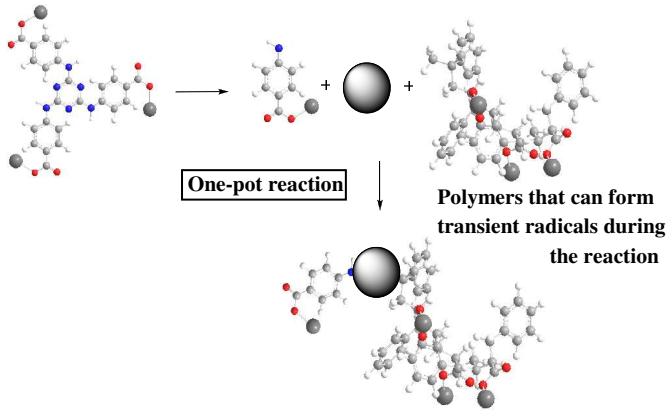


Scheme 2. Protocol A from S.M.A.R.T. 4000

Protocol B involves a tris reagent of choice and a free-standing polymer that is added to the reaction mixture during the milling process. The polymer used in this protocol needs to have the ability to form radicals that can subsequently react with the surface of the pigment. One can envision many different classes of polymers that can form transient radicals and have the potential to be attached to the surface such as styrene-acrylic copolymers, styrene-maleic anhydride copolymers, polyurethanes etc. The versatility of this process gives us the ability of having a "tool kit" approach to develop different dispersions for different applications.

The process of incidental attachment can even use mixtures of polymers, introduced at the same time or sequentially in the reaction in order to modulate the properties of the pigment. Using this technology, we have successfully made stable dispersions with 1, 3, 4 and even 5 different polymers (see the Results section).

The resulting pigment dispersions are subjected to the ultrafiltration purification step that removes the salts and the "free" or unattached polymer.



Scheme 3. Protocol B for S.M.A.R.T. 4000

Results

Protocol A

Sensijet® Black SDP 1000 was treated with tris reagents containing amino-PEO or amino-PPO chains and the resulting purified dispersions were analyzed by X-RAY Photoelectron Spectroscopy (XPS) [4]. The results in Table 2 indicate a clear change from the starting dispersion, in this case the Na + K content decreased due to the introduction of non-ionic polymers.

Table 1. Examples of S.M.A.R.T. 4007 dispersions obtained using Protocol A

Label	Tris substituents
Carbon [21]	1x Surfonamine B-30 +2x 4-ABA
Carbon [27]	1x Surfonamine B-60 + 2x 4-ABA
Carbon [29]	1x Surfonamine B-30 + 2x Surfonamine L-100
Carbon [31]	3x Surfonamine B-60
Carbon [33]	3x Surfonamine B-30

Table 2. XPS Surface Concentrations of Carbon Black Samples (Atomic %).

Sample	C	N	O	Na	Cl	K
Carbon - untreated	97.5	-	2.4	-	0.03	-
SDP1000	81.4	-	13.0	5.3	0.19	-
Carbon [21]	79.6	2.6	13.2	3.5	0.30	0.7
Carbon [27]	78.8	0.5	15.1	4.7	0.14	0.8
Carbon [29]	79.0	1.4	14.9	3.9	0.26	0.5
Carbon [31]	80.0	0.3	13.8	4.9	0.11	0.9
Carbon [33]	80.7	1.0	13.5	3.9	0.11	0.7

The increase in N surface concentration is also a strong indicator for the attachment through nitrogen linkage. Below are the types of nitrogen linkages detected on the surface of carbon pigment after the modification.

Table 3. Nitrogen chemistries

Sample	N-C=N	NH
Carbon untreated	-	-
SDP 1000	-	-
Carbon [21]	49	51
Carbon [27]	48	52
Carbon [29]	45	55
Carbon [31]	42	58
Carbon [33]	43	57

Protocol B

Colored and black raw pigments were treated using this methodology with styrene-maleic anhydride (SMA) Mw 1700 at 20% (based on pigment, bop) in the presence of tris 4-ABA. The resulting dispersions were purified through ultrafiltration. These dispersions are stable upon incubation at 70°C for 4 weeks (i.e. average particle size and viscosity increased less than 10% from original values). XPS results shown in Table 4 indicate the attachment has occurred based on increased Na+K concentration and a clear change in C, N and O content compared to the untreated pigments.

Table 4. XPS Surface Concentrations of Several Types of S.M.A.R.T. 4000 Pigments Modified with SMA (Atomic %).

Sample	C	N	O	Na+K	S
PB 15 - untreated	78.7	17.3	1.6	0.1	0.09
PB 15 + SMA [05]	70	13.1	10	4.2	0.25
PR 122 - untreated	84.4	8	7.7	-	-
PR 122 + SMA [57]	82	6.1	10.2	1.6	0.14
PY 74 - untreated	64.6	13.8	20.8	0.3	0.3
PY 74 + SMA [49]	69.6	9.5	19.1	1.6	0.1
Carbon - untreated	97.5	-	2.4	-	0.11
Carbon] + SMA [51]	83.3	2.4	9.3	3.9	0.8

Following the same Protocol B, several multi-polymer dispersions were made using polymers from 3 different classes: styrene-acrylics, polyurethanes and styrene-maleic anhydrides. They were chosen to cover a wide range of molecular weights (Mw from 4900 to 200k), acid numbers (An from 53 to 465) and glass transition temperatures (Tg from -16°C to 128°C). All the dispersions showed high thermal stability upon incubation at 70°C for 4 weeks. Based on UV-VIS absorption at 420 nm, we calculated the concentration of polymer remaining on the carbon after purification and the results are shown in table 5. This data indicates that a considerable amount of polymer was attached. Small amounts of polymers that did not attach to the surface were removed during ultrafiltration

Several physical properties of these dispersions are listed in Table 6. Note the relatively low viscosity of the dispersions, a key advantage of attaching the polymers to the surface of the pigment instead of just adding it to the dispersion.

All dispersions reported in Table 6 had particle sizes of 94-113 nm but larger particle sizes are easily obtained by changing the starting material and the reaction and milling conditions. Table 7 describes two black S.M.A.R.T. 4007 dispersions that have larger z-average particle size obtained through such modifications.

Table 5. Examples of multi-polymer S.M.A.R.T. 4007 dispersions obtained using Protocol B

Sample	Polymers	% Solids	% Polymer used in reaction (bop)	% Attached Polymer (bop)
Carbon [61]	B, C, D, H, G	13.1	32	26.9
Carbon [63]	A, C, H, F, G	12.9	32	25.8
Carbon [65]	A, D, E, H	13.0	29	23.7
Carbon [67]	A, C, D	13.0	26	14.9
Carbon [69]	B, C, F	12.1	26	26
Carbon [71]	B, D, E, G	13.0	29	17.5
Carbon [73]	B, E, H, F	12.8	29	27.8
Carbon [75]	A, E, F, G	13.3	29	19.9

Table 6. Physical Properties of the Multi-polymer S.M.A.R.T. 4007 Pigments.

Sample	Visc (cps)	Cond (mS)	ST (dynes /cm)	Zeta potential (mV)	Particle size avg. (nm)
Carbon [61]	1.96	3.74	57	-68.9	113
Carbon [63]	1.88	3.3	54	-69.6	111
Carbon [65]	2.52	2.9	60	-67.4	110
Carbon [67]	2.08	2.86	53.8	-67.9	97
Carbon [69]	2.1	3.6	46.4	-72.1	106
Carbon [71]	2.26	3.96	49.1	-65.3	111
Carbon [73]	2.23	3.27	51.3	-62.3	110
Carbon [75]	2.25	3.04	44.4	-69.9	94

Table 6. Physical Properties of the larger size S.M.A.R.T. 4007 Pigments.

Sample	Visc (cps)	Cond (mS)	ST (dynes/ cm)	Zeta potential (mV)	Particle size avg. (nm)
Carbon [81]	1.72	1.67	61	-67.4	128
Carbon [83]	2.32	2.26	55.8	-69.4	119

Conclusion

Sensient has developed a tool-kit approach to produce S.M.A.R.T. 4000 pigments with polymer attachment. This technology is able to deliver a broad range of products that can be customized for different inkjet applications with specific requirements of image quality and durability.

References

[1] US20090050014A1

[2] P.K. Sujeeth, Dan Oullette, Mark Ulrich, and John Kane, Sensient's Suite of Self-Dispersed Color Nano Particle Dispersions – 1,3,5-Triazine Derivatives as Versatile Intermediates for Attachment on Pigments, Proc. NIP25, pg. 265 (2009).

[3] US20100061951A1

[4] XPS work done by Evans Analytical Group, Chanhassen MN

Author Biography

Mihaela Madaras completed her graduate education at the University of North Carolina at Chapel Hill. She worked at Eastman Kodak Co. for 10 years where she focused on the synthesis, characterization, and formulation of new dyes and pigments for inkjet. In 2009 she joined Sensient Technologies and she is currently involved in the development of new self-dispersed pigments with improved performance for inkjet.