Sensient's Suite of Self-Dispersed Color Nano Particle Dispersions - 1,3,5-Triazine Derivatives as Versatile Intermediates for Attachment on Pigments

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Abstract

Small organic molecules such as sulfanilic acid and 4-aminobenzoic acid are directly attached to the pigment surface by a process involving cyanuric chloride and the corresponding amino acid. The intermediate, a substituted amino-1,3,5-triazine derivatives undergo facile disproportionation when treated with a radical initiator (potassium persulfate) and facilitate the attachment of the organic molecules on the pigment surface. The surface modification achieved by this process is as versatile as the well established diazonium decomposition pathway without the low pH requirement and the potential explosion hazards.

This process can be expanded to attach small molecular weight polymers containing an amino end group – examples are poly(ethoxy, propoxy)amines such as Surfonamines. The radical pathway can be exploited to attach other polymers such as poly (styrene-co-maleic anhride) or SMA resins. The ability to attach groups at neutral and basic pH can be exploited to include resin stabilized nano dispersions as the pigment source and skip the milling step usually associated with such a process. This attachment methodology enables customization of pigment surfaces to suit a broad range of applications and ink requirements.

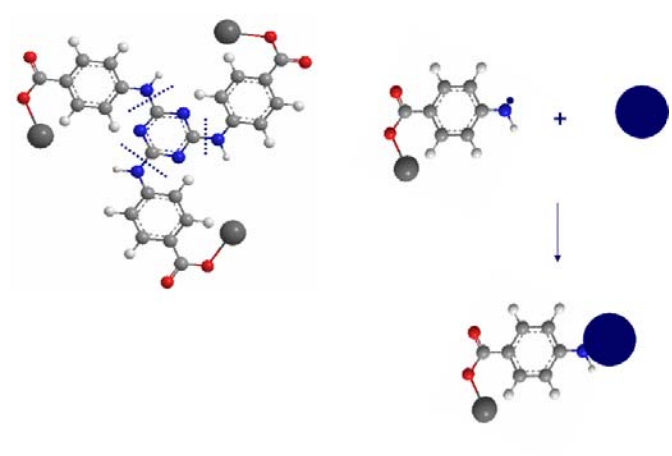
Discussion:

Advances in digital printing have resulted in innovation across the board in the printing arena. Innovative solutions are being sought from the ink manufacturers. There is an increased need for quick drying, storage stable, vibrant inks particularly with the advent of the pico-liter delivery capable print heads and single pass printers. To enable the development of inks that can meet such demands, the surface modified pigment dispersions have to have a much smaller and narrower particle size distribution and be stable under extreme storage, shipping and usage conditions. Moreover, to satisfy the requirement for greater durability and line print quality, ink formulators are looking for help from customized surface modification technologies. Specifically pigment dispersions with surface modified by organic group attachments are being looked at with great interest by many ink technologists. Addressing this need, Sensient has developed a technology portfolio, a sort of "tool-kit" for ink technologists.

Sensient chemistry[1] utilizes well known reactive dye chemistry to build a set of reagents capable of inserting target molecules on the surface of a pigment particle. The highly reactive cyanuric chloride, a key intermediate in building reactive dyes is used to make Tris-substituted amino-1,3,5-triazine intermediates or just "Tris reagent". The reaction to form such intermediates is quite simple and is done in aqueous media. It is quite safe and is easily scaled to production quantities with existing plant equipment. Moreover, such reagents can be formed under wide range of pH making it suitable to form a wide array of Tris reagents.

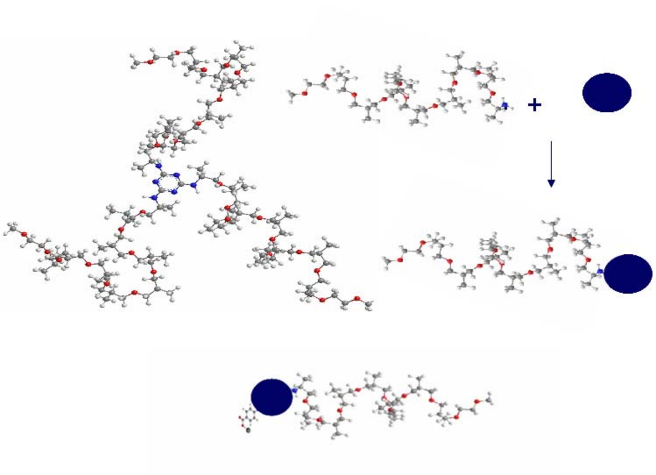
The reagents are used as is without any purification and are mostly consumed during a radical initiator assisted disproportionation reaction. This makes the process to be classified as "eco friendly" and safe as the exposure to the worker and the environment of any new chemical is kept to a minimum.

Formation of Tris 4-aminobenzoic acid reagent and its utilization as an intermediate to attach an aminobenzoic acid group on the surface of a pigment is depicted below (Scheme I). Sensient has successfully demonstrated the utility of this process when done inside any milling equipment to form highly stable (via negative charge groups from surface carboxylates) pigment dispersions meeting the demanding specifications as outlined earlier. Aminobenzene Sulfonic acid (Sulfanilic acid) can also be used to attach in similar manner Aminobenzene Sulfonic acid groups.



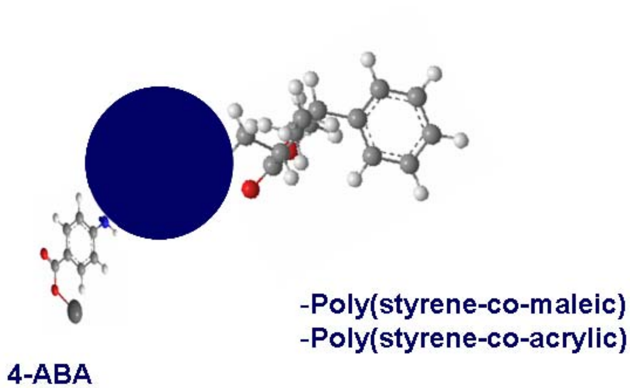
Scheme I

The versatility of this approach is evident when one considers the numerous options available to modify the pigment surfaces by this methodology. Sensient's approach to meet the increasing demands of the industry is to offer this technology as a "tool-kit" rather than provide a compound specific solution. For example if there is a need to attach a bulky neutral group as a spacer interspaced with stabilizing small organic groups, it can be easily accomplished by using a combination (mixed) approach. The idea is to make a Tris reagent using a suitable commercially available polyethoxy polypropoxy long chain amine and use it mixed mode with either 4-aminobenzoic acid Tris reagent [4-ABA] or 4-aminobenzene sulfonic acid Tris reagent [SA]. It is also possible to build a mixed tris reagent containing both the polymer chain and the amino acid as shown in Scheme II.



Scheme II

A third option available using this Sensient "tool-kit" is to avail incidental radical formation with appropriate polymers. For example, the use of a poly (styrene-co-maleicanhydride) [SMA] resin in conjunction with the Tris-reagents has been found to be a useful way to simultaneously attach the amino acid and the polymer in one pot reaction as shown in Scheme III.



Scheme III

The general approach is to stabilize the pigment particle with amino acid attachments and offer a secondary attachment mechanism to achieve the same benefits from ingredients in a typical ink formula by doing so. Unlike an additive which may or may not be associated with the pigment particle all the time, the attachment forces such group to be always present on the particle. The beneficial effect of this is the ability to minimize the usage and thereby have a better control on the physical properties of the final ink and be able to control the viscosity, surface tension etc., for media independence and better jettability and durability properties.

Results:

The building of Sensient tool kit starts with the preparation of the Tris reagents. This is done in single pot reaction starting with ice water slurry of cyanuric chloride. A buffered solution of the substrate, usually a compound with amino end group is added to the cyanuric chloride slurry and the nucleophilic displacement of the three chlorines in the cyanuric chloride is facilitated by heat. The displacement of the third chlorine takes prolonged heat above 90 °C. In most cases the progress and consumption of the amino substrate can be monitored by HPLC or similar methods. During the reaction, the mixture goes through several changes and finally becomes a clear transparent liquid. This mixture can be concentrated to desired level (usually 10-15%) and stored indefinitely.

Tris reagents are good wetting agents for the pigments by themselves. Other wetting agents can be used to enhance this process. During this process it is beneficial to initiate the attachment process to lower the viscosity and improve the wetting process. This is done with the help of a radical initiator such as potassium persulfate at about 50 °C. The attachment and particle size reduction is done simultaneously as the next step in a milling device. At the end, any unattached organic molecules and byproducts such as inorganic salts are removed by standard ultrafiltration process. The product is then concentrated to the final strength and larger particles are removed through conventional methods. Stable dispersions with a mean particle size distribution around 100 nm have been produced by this method.

The demonstration of the expanded Sensient "tool-kit" to include incidental attachment with an SMA type resin was completed recently. As expected the final dispersion showed enhanced properties due to the presence of SMA groups which if not attached, would have been removed during the purification process.

The attachment of the target molecules on the pigment surface was confirmed by X_Ray Photoelectron Spectroscopy[2] (XPS). The degree of attachment was also established by elemental analysis of the dried, treated pigment after purification. The near 1:1 ratio of N to Na in modified carbon samples is an indication that the majority of stabilizing group is derived from aminobenzoic acid even though a radical process could lead to other forms of attachments. The surface concentration of elements (Atomic %) does not correlate well with the bulk composition obtained by elemental analysis of a dried sample. This is only to be expected. XPS analysis should be taken as the proof of attachment as it measures the energy required to break the type of bonds. The results of CHN, S and Na analyses do support the assumption that to get a particle sufficiently charged we will need about 1:10 ratio of attaching species to pigment molecules.

Table I
XPS Surface Concentrations (Atomic %)

Example	C	N	O	Na	S
C-SA [49]	90.1	1.4	6.8	0.8	0.7
C-ABA [71]	70.3	2.7	20.9	2.2	0.2
PB15-SA [35]	78.4	15.9	2.9	0.4	0.4
PB15-ABA [59]	78.0	16.2	2.9	0.3	0.2
PR122-SA [80]	83.1	7.9	8.4	0.2	0.3
PR122-ABA [20]	83.1	7.6	8.8	0.15	0.05
PY74-SA [32]	63.2	13.8	21.6	0.4	0.4
PY74-ABA [38]	56.4	11.2	27.1	0.5	0.3

Table II
XPS Results – Carbon Chemistries (% of total C)

Example	C-C,H	C-O/C-N/N-C=N/C_2NH	COONa/ CSO_3Na
C-SA [49]	90	3	1.4
C-ABA [71]	88	4	6
PB15-SA [35]	72	20	0.8
PB15-ABA [59]	70	22	0.7
PR122-SA [80]	68	25.6	2.0
PR122-ABA [20]	66	25.5	2.1
PY74-SA [32]	44	51	2.1
PY74-ABA [38]	45	50	2.5

Table III
XPS Results – Oxygen Chemistries (% of total O)

Example	C=O, COONa, SO_x	C-O	Other
C-SA [49]	62	38	-
C-ABA [71]	60	40	-
PB15-SA [35]	65	35	-
PB15-ABA [59]	57	43	-
PR122-SA [80]	67	24	10
PR122-ABA [20]	60	32	11
PY74-SA [32]	42	58	-
PY74-ABA [38]	45	55	-

Table IV
XPS Results – Nitrogen Chemistries (% of total N)

Example	N-C=N	NH(Aromatic Shake-up)	NO_3/ CN-Cu
C-SA [49]	54	46	-
C-ABA [71]	46	54	-
PB15-SA [35]	78	15	7
PB15-ABA [59]	81	8	11

In the following table (Table V), the CHN and S analyses[3] from dry powders and the Na/K analysis based on solids of the dispersion by Ion Chromatography is compiled for comparison. The combined Na and K values are taken as measure of negative charge groups (carboxyl or Sulfonic) attached to the surface. Since a triazinyl group is attached, the total nitrogen per attaching group has to be four times of the acidic group. Based on the values reported, it is safe to conclude that most of the groups are attached directly as –NH-benzene carboxyl/sulfonic acid.

Table V
Elemental analysis (% C,H,N,S,Na,K)

Example	C	H	N	S	Na	K
C-SA	85.25	0.88	0.91	1.13	0.57	0.59
C-ABA	80.87	1.36	1.61	0.33	0.29	0.3
PB15-ABA	65.95	3.15	18.82	0.54	0.2	0.07
PR122-SA	74.93	4.70	8.00	0.36	0.14	0.07
PR122-ABA	75.74	4.54	8.09	0.20	0.11	0.16
PY74-SA	52.75	4.63	13.49	0.57	0.46	0.35
PY74-ABA	52.56	4.66	13.40	0.53	0.24	0.47

For an ink chemist, the value of the treatments (attachments) on the pigment surface is apparent only when the dispersions are stressed under extreme conditions and the physical properties are measured. A good dispersion should have minimal change after weeks of heat stress at 70 °C. The table below gives the results of change in viscosity, particle size and pH.

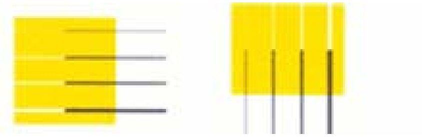
Table VI
Stability Data

Example	Viscosity (cPs)			pH	
	Initial	Week 1	Week 3	Initial	Final
Carbon	2.66	2.67	3.22	9.4	9.1
PB 15 :3	1.78	1.78	1.81	8.0	8.0
PY74	1.7	1.7	1.6	7.8	7.3
Example	**Particle Size (D50 : nm)**				
	Initial	Week 1	Week 3		
Carbon	110	115	113		
PB 15 :3	157	156	156		
PY74	173	153	155		

These dispersions were grouped on the basis of attaching groups and were used to make two inksets. First one (BA3) used dispersions modified by attaching 4-aminobenzoic acid and the second set (SA3) consisted of dispersions made by attaching Sulfanilic acid group. Inks were also made using commercially available self dispersed pigments for comparison (control). The print samples on four different copy papers were sent to Rochester Institute of Technology[4] for evaluation. These results are below as Graph 1 thru 5.

Graph 1 (Line Quality/Bleed)

Evaluation Method: RIT Inkjet Image Quality Protocol
Samples: 3



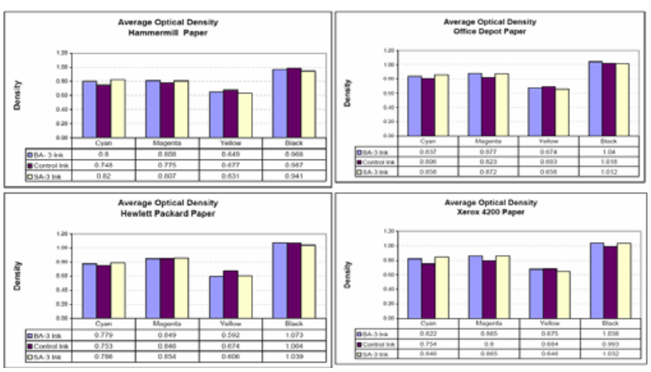
Horizontol Line Bleed/Raggedness (mm) Hammermill Paper			
Measurement	**BA-3 Ink**	**Control Ink**	**SA-3 Ink**
Black on Yellow Bleed (4 pixel line)	0.005	0.018	0.013
Black on Yellow Average Raggedness	0.018	0.021	0.020
Black on Paper Average Raggedness	0.017	0.017	0.019

Horizontol Line Bleed/Raggedness (mm) Hewlett Packard Paper			
Measurement	**BA-3 Ink**	**Control Ink**	**SA-3 Ink**
Black on Yellow Bleed (4 pixel line)	0.006	0.007	0.006
Black on Yellow Average Raggedness	0.012	0.014	0.013
Black on Paper Average Raggedness	0.011	0.013	0.012

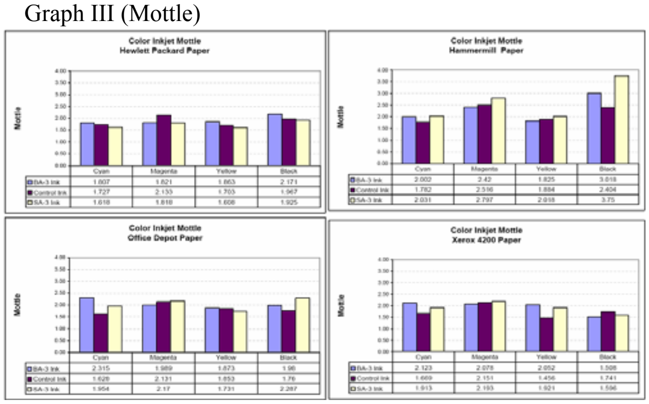
Vertical Line Bleed/Raggedness (mm) Hammermill Paper			
Measurement	**BA-3 Ink**	**Control Ink**	**SA-3 Ink**
Black on Yellow Bleed (4 pixel line)	-0.004	-0.013	-0.002
Black on Yellow Average Raggedness	0.016	0.020	0.016
Black on Paper Average Raggedness	0.015	0.018	0.017

Vertical Line Bleed/Raggedness (mm) Hewlett Packard Paper			
Measurement	**BA-3 Ink**	**Control Ink**	**SA-3 Ink**
Black on Yellow Bleed (4 pixel line)	-0.002	0.001	-0.008
Black on Yellow Average Raggedness	0.014	0.017	0.016
Black on Paper Average Raggedness	0.015	0.015	0.014

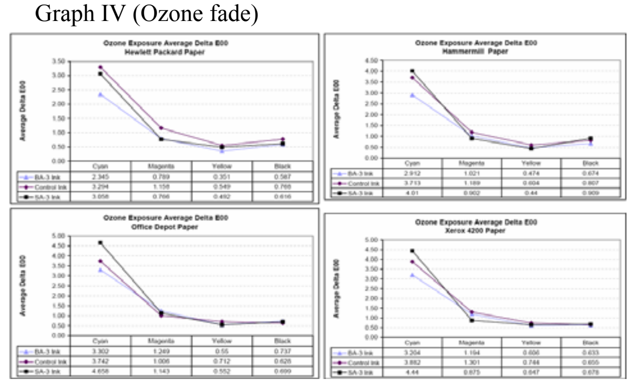
Graph II (OD)



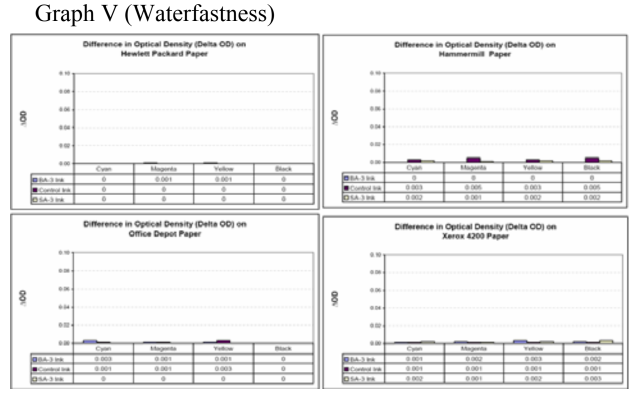
Graph III (Mottle)



Graph IV (Ozone fade)



Graph V (Waterfastness)



Conclusion:

Sensient has developed a versatile "tool-kit" with the use of amino-1,3,5-triazine derivatives to attach a wide range of organic molecules including polymers. This attachment methodology enables customization of pigment surfaces to suit a broad range of applications including specific ink requirements that addresses increasing demands for stability, permanence and jetting performance.

References

[1] UA 20090050014A1.
[2] This work was done by Evans Analytical Group, Chanhassen, MN.
[3] CHN and S analysis was carried out by Schwarzkopf Microanalytical Laboratory. Inc., Woodside, NY.
[4] Imaging Products Laboratory, Rochester Institute of Technology, Rochester, NY.

Author Biography

Dr. Sujeeth joined Sensient Colors Inc. in 1984 and is now director of R&D, responsible for the research and development efforts of Sensient Technical Colors. Dr. Sujeeth's recent work lead to the successful development of several commercial, patented technologies for self-dispersing black and color pigments which is marketed under brand name Sensijet® SDP dispersions.

Dr. Sujeeth is a long standing member of American Chemical Society and has a Ph.D. in organic chemistry from Indian Institute of Technology, Madras, India.