Conventional Surface Treatment of Pigment for Digital Imaging Application

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Abstract

A wide range of chemical affinity control of pigment surface against media, such as high polar solvents including water, lower alcohols and ketones, and low polar solvents involving toluene was demonstrated by utilizing organohalosilane/halosilane containing a number of carbons from zero to 18 onto the surface of pigment. The treatment was accomplished with an environmentally friendly process while keeping the pigment particle size fine and its distribution narrow. The efficiency of the surface modification with those silanes did not show a big influence caused by varying chemical property of pigment surface. High technical feasibility of the treatment for digital imaging applications is suggested.

Introduction

Many kinds of pigments in large quantity are in use for diversified Digital Imaging Applications lately. The requirements of the digital imaging applications to those pigments are quite widely different in their chemical properties. A commonly taken methodology to solve these problems is the surface modification of the pigment in a medium with “surfactant(s)”. However, it requires a large amount of time to search the surfactants for each pigment because each pigment exhibits different chemical nature. Particle size and chemical resistance of the pigment are other factors to be considered for designing the pigment involved products. Therefore, factors to modify the pigment for digital imaging applications are revealed as follows: 1) simple procedure in a short time, 2) stable fixation of surface modifying agent on surface of the pigment, 3) single concept of chemistry modifying almost all pigments for a wide range of digital imaging applications, 4) applying low grinding power and time, 5) low dependency on surface character of pigment and 6) environmentally friendly process. It is well known that polysiloxane materials have many useful attributes, such as surface tension energy reduction, dispersion ability, high heat resistance, high chemical resistance, excellent adhesion property and good weatherability. Moreover, chemical affinities of the polysiloxane materials matching the requirements for digital imaging systems will receive contributions from nature of organic moieties attached onto silicone atoms involved in the polymer main chains. A scheme of the designed surface coating process, involving an interfacial chemical reaction, for the pigment with the siloxane material is as follows:

Organohalosilane/Halosilane + Water =
Poly(organo/siloxane)

The poly(organosiloxane) will adhere on the surface of the pigment in water, if the pigment is involved in the system. Furthermore, polarity of the surface will be controlled by selecting organic moiety attaching onto a silicone atom.

Experimental

Process Equipment

A 1.2 or 5 liter stainless steel container equipped with a disperser from Premeir Mill Corp., Laboratory Dispersator, Series 2000, Model 90 with 2.5 inch blades, and a hot plate was used for all processes.

Pigments

A presscake, Copper Phthalocyanine Blue G/S (C.I. Pigment Blue 15:3) is from Magruder Color Co., Inc. Alkali Blue (C.I. Pigment Blue 19) in presscake form is from BASF.

Carbon black (C.I. Pigment Black 7) in pre-ground slurry form with water, AJACK BLACK 5021, from Dispersion Solution Inc. is evaluated. Titanium dioxide (C.I. Pigment White 6) in dry powder form from Nanophase is also employed.

Surface-Modifying Agents

Monoorganotrichlorosilanes are from Gelest, Inc. Tetrachlorosilane is from Aldrich Chemical Co.

Surface Modification Procedure

Pigment Blue 15:3 (for Table 1). A slurry (10 wt.% of pigment) was reconstituted from a presscake (36 grams of pigment in dry weight) with water in the container. It was mixed well with the disperser at app. 1000 rpm for 20 minutes. A surface-modifying agent was introduced into the slurry slowly at high speed dispersing condition between 2000 rpm and 3000rpm. After the addition of the surface-modifying agent into the slurry, the mixture was heated up to about 60 degrees C while keeping the high speed dispersing condition at 3000 rpm for 30 minutes. Then the hot plate was removed from the reaction set and the mixture was cooled off by air while mixing at 2000 rpm. The surface treated pigment slurry was split in two and put in two 1-quart jars. About 200 grams of ethanol were added to the slurry in the jar and they were shaken by hand. After the treated pigments settled, the supernatant was decanted and the slurry was air-dried on watch-glasses from overnight up to 3 days. The addition of ethanol caused elimination of a certain amount of water from the slurry and accelerated the evaporation speed of water from it. The dried surface treated pigment was broken off by using a spatula in an 8 oz glass jar. A control indicated by 0 wt.% in Table 1 was prepared by using Copper Phthalocyanine Blue G/S with the drying and breaking procedures described above.

Pigment Black 7, Titanium Dioxide and Pigment Blue 19 (for Tables 2, 3 and 4). Slurries, 360 grams, (10 wt.% for Pigment Black 7 and Pigment Blue 19, and 20 wt. % for Titanium Dioxide) were reconstituted by using those pigments in water (for Pigment Black 7 and Pigment Blue 19) or ethanol (50 wt.%) involved aqueous solution (for Titanium Dioxide).

After mixing the slurry with the disperser at app. 1000 rpm for 20 minutes, the surface-modifying agent, $SiCl_4$ (6.5 wt.% for Pigment Black 7 and Pigment Blue 19, and 10 wt.% for Titanium Dioxide), was added into the slurry slowly while mixing at 3000 rpm. The temperature of the slurry was kept at room temperature until the addition of the agent was completed. It then was increased up to 70 degrees C for a water based slurry. The temperature was controlled at around 50 degrees C for a mixture of water and ethanol based slurry. Those slurries were mixed at 3000 rpm at the same temperature for 30 minutes. Subsequently, the slurries were cooled to near room temperature while mixing at around 2000 rpm.

The slurry with the surface modified pigment was filtered through a filter paper, and pH of the filtrate was evaluated by using a pH meter. The residue on the filter paper formed a cake.

pH adjustment was carried out by the following procedures: 1) A cake consisting of the surface modified pigment and water or a mixture of ethanol and water, about 50 grams, was re-dispersed in water in a ratio of 1/5 (cake/water) by weight. 2) Diluted ammonium hydroxide in water was dropped in the slurry with stirring and pH of the slurry was checked by using pH paper. 3) When the pH value reached around 10, the addition of the ammonium hydroxide was stopped. After filtration of the slurry and additional washing with deionized water (100 mL, twice of the washing), pH of the filtrate was measured by using pH meter.

Controls indicated by 0 wt.% in the tables were prepared by using a filtered cake for AJACK BLACK 5021, dry powder of Titanium Dioxide and a presscake for Alkali Blue without any surface treatments.

Tests on Identifying Influence of Carbon Chain Length (for Table 5). Carbon black dispersed solution, 2000 grams, containing 1.7 wt. % of carbon black was prepared in a 5 liter container by using AJACK BLACK 5021 and water.

After mixing the carbon black dispersion at app. 1000 rpm for 20 minutes, the surface-modifying agent (11.8 m mole) was added into the dispersion slowly while mixing at 3000 rpm. The temperature of the dispersion was kept at room temperature until the addition of the agent was completed. Then it was increased up to 60 degrees C while keeping the high speed dispersing condition at 4000 rpm. The dispersion was mixed at 4000 rpm at the same temperature for 30 minutes. Then, it was cooled to near room temperature while mixing at around 2000 rpm.

Subsequently, the pH of the dispersion was adjusted by using ammonium hydroxide aqueous solution at around 8.0. Then the dispersion was filtered and washed as described above. The residue, cake, was air-dried for 3 days and pulverized by using a coffee bean grinder for home use.

Proportion of Surface Treating Agent Applied onto Pigment Surface.

The proportion is indicated as “wt. %”, that means ratio of agent/(agent+pigment) by weight, in Tables 1 through 4.

Affinity Test

Pigment Blue 15:3 (for Table 1). A pigment dispersion, 10 grams, involving app. 1 weight % of the pigment in dry form and a solvent, was prepared in a 20 mL glass vial with sonication for about 20 minutes. The vial was kept still on a table for 24 hours, and the degree of suspension stability of the pigment in the solvent was evaluated as follows; E: Suspended very well with no settling, G: Suspended well with a little settling, P: Poorly suspended with a large settling, VP: Completely settled, and F: Floating.

Pigment Black 7, Titanium Dioxide and Pigment Blue 19 (for Tables 2,3 and 4). Approximately 1 wt. % of pigment in cake form or, as a control, pigment supplied in dry form, was dispersed in a solvent placed in a 20 mL glass vial. It was sonicated for 10 minutes. After the preparation, the dispersion was kept still on a bench for 24 hours and then the stability of the dispersed pigment in the solvent was evaluated by observing the amount of settled pigment as described above.

Tests on Identifying Influence of Carbon Chain Length (for Table 5). Surface modified carbon black in pulverized dry powder form, 5 wt. %, in a solvent was placed in a 20 mL glass vial and the mixture was sonicated for 20 minutes. Then, the dispersion in the vial was kept still on a bench for 2 to 3 weeks. Procedure of evaluating its suspended stability is described above.

Particle Size Analysis

A laser beam scattering particle size analyzer from HORIBA, Model LA-900 (range of particle size detection: 0.05 micrometers to 1000 micrometers), was employed for the particle size distribution study on the surface treated pigments and their controls that were dispersed in ethanol. Procedures for preparing pigment dispersions are described in the section on Affinity Tests. M.D. and S.D. show

Median Diameter and Standard Deviation in a unit of micrometer respectively.

Results and Discussion

Copper phthalocyanine blue (C.I. Pigment Blue. 15:3) is one of commonly used pigments in graphic art technologies. It exhibits quite high hydrophobic property on its surface. Therefore, it needs interfacial modification when it faces into high polar or hydrophilic medium with the expectation of a good performance. Table 1 shows a possibility of converting the pigment surface character completely into the opposite direction by using a conventional technique. These tests do not involve pH adjustment after the surface modifications were completed.

Table 1. Affinity Tests on Surface Modified P.B. 15:3

R* (wt%)	CH3 (0)	CH3 (5)	CH3 (10)	Cl (6.5)
H2O	P	G	G	E
EtOH	VP	G	G	E
MEK	VP	VP	VP	VP
M.D.	0.205	0.101	0.210	0.126
S.D.	1.738	0.085	0.898	0.072

*: R-SiCl3 as surface modifying agents

It is clear that the quantity of loading the agent and selecting the nature of the agent are the big factors to match the interfacial affinity of the pigment surface against solvents in keeping particle size small and its distribution narrow.

Carbon black (C.I. Pigment Black 7) is the most commonly used pigment, which exhibits medium to high degree of hydrophobic property based on the degree of volatile materials involved in the pigment, in the reprographic market. A pre-ground carbon black involved slurry with water was selected for these tests.

The pre-ground carbon black in slurry form, AJACK BLACK 5021, treated with hydrolyzed SiCl4 indicated significant pH dependency on its interfacial affinity against the three polar solvents besides keeping its particle size and distribution quite small and narrow with pH adjustment. (See Table 2.)

Table 2. Affinity Test on Surface Modified Carbon Black and influence of pH

SiCl4 (wt%)	0	6.5	6.5
pH	4.28	2.68	7.94
H2O	P	E	VP
EtOH	E	VP	E
MEK	E	VP	E
M.D.	0.110	0.252	N/A*
S.D.	0.194	0.632	N/A*

*: N/A because of no detection performed by the particle size analyzer.

Titanium oxide is a well known white inorganic pigment used for a wide range of coloring applications. However, its specific gravity is considerably higher than those of commonly used solvents. Therefore, suspending titanium oxide pigment in a low viscous fluid is a big technical challenge.

Table 3. Affinity Tests on Surface Modified TiO2 and Influence of pH

SiCl4 (wt%)	0	10	10
pH	2.21	0.65	7.97
H2O	VP	E	E
EtOH	E	P	E
MEK	VP	VP	G
M.D.	0.107	0.106	0.104
S.D.	0.478	0.415	0.025

The pigment without surface modification revealed a rather acidic (pH=2.21) nature on its surface character. It is clear that pH adjustment after the surface modification process increased interfacial affinity of the pigment against the three polar solvents with excellent particle size and distribution. (See Table 3.)

Alkali Blue pigment (C.I. Pigment Blue 19) has strong ionic and hydrophilic properties and is known as a tough pigment to be ground once it is dried.

Table 4. Affinity Tests on Surface Modified Alkali Blue and Influence of pH

SiCl4 (wt%)	0	6.5	6.5
pH	1.55	1.01	8.10
H2O	VP	VP	E
EtOH	E	E	E
MEK	VP	P	E

Affinity of the pigment, with and without surface modification using hydrolysis of SiCl4, and with and without pH adjustment, against ethanol came out quite high because of high affinity of chemical nature of the pigment to ethanol. The surface modified pigment with pH adjustment at pH8.10 showed quite high dispersing capability into water and MEK. (See Table 4.)

It is assumed that extension of carbon chain length attaching onto a silicon atom will increase hydrophobic property of poly(organosiloxane) on pigment, that is, the influence of the chain length will be shown in the interfacial affinity change from polar to non-polar solvents.

Influence of carbon chain length involved in the interfacial layer on the carbon black surface on varying affinity against solvents came out quite clearly as follows: 1) Shorter chain length (n = 0 to 2) indicated high affinity against polar solvents. 2) Longer chain length (n = 7 to 18) showed excellent affinity against low polar solvent, such as toluene, besides showing good affinity to ethanol and acetone. 3) Soy oil was able to suspend carbon black pigment with most of hydrolyzed surface-modifying agents except the ones (n = 0 to 2 and t-4) because of its relatively high viscosity compared with the others and its acid value, app. 2. (See Table 5.)

The reason for the second fact described above, relating to high affinity to ethanol and acetone, is not clear yet.

Table 5. Influence of Carbon Chain Length Involved in Surface Modifying Agent Applied on Carbon Black Pigment (pH adjusted in a range of 7.0 and 8.5)

n*	H2O	EtOH	A	T	M	Soy
0	VP	E	E**	-	-	-
1	VP	E	E**	-	-	-
2	P	E	E	VP	VP	VP
3	P	VP	P	VP	VP	E
4	P	VP	VP	VP	VP	E
t-4	VP	VP	G	VP	VP	VP
5	G	VP	VP	P	VP	E
6	F	VP	VP	G	VP	E
c-6	G	VP	VP	VP	VP	E
7	F	E	VP	E	VP	E
8	F	E	G	E	VP	E
10	F	E	E	E	VP	E
18	F	VP	E	E	VP	E

n*: Number of carbon atoms involved in organic moiety as R attaching onto silicon atom (R-SiCl3).

n=0: SiCl4 (14.7 m mole, 6.5 wt.%) was applied for AJACK BLACK 5021, n=1: CH3SiCl3 (60 m mole, 20 wt.%) was applied for Panther 17 V in dry powder form from Engineering Carbon. Procedures for evaluating these samples were described in the section involving Pigment Black 7.

A: Acetone, T: Toluene, M: Magiesol 44, and Soy: Soy Oil

**: MEK as solvent.

t-4: tert-butyl, c-6: cyclohexyl

Application for Digital Imaging Systems

The conventional surface modification technology may fit into digital imaging systems, such as inkjet printing systems involving drop-on-demand and continuous systems, electrophotography, electrostatic imaging systems, magnetography wax type thermal transfer printing system and digital duplicator, because of a high degree of polarity variation capability with excellent pigment particle size and distribution for these systems.

Conclusions

Poly(organosiloxane) generated by hydrolysis of organohalosilane or halosilane as a surface modifying agent adhered well onto the surfaces, which have a wide range of chemical property variation, of pigments and exhibited capability of adjusting the factor of hydrophilic/hydrophobic property by varying the organic moiety attached onto a silicone atom involved in the agent. Furthermore, the surface modification technology demonstrated ability to be operated under environmentally friendly process and to keep particle size and distribution of pigment fine and narrow respectively without applying major pigment-grinding process. This is a work made for Videojet Systems International, Inc.

References

1. Yoshikazu Mizobuchi, Method for treating pigment particles to improve dispersability and particle size distribution, WO 98/32801.

Biography

Dr. Yoshikazu Mizobuchi is currently Senior Staff Chemist in the Department of Chemical Development of Videojet Systems International, Inc. He is responsible for chemical research, development and supervising group members. He received his Ph.D. in Applied Chemistry from Osaka University, Osaka, Japan, in 1981. He has had experience as a post-doctoral research associate at the University of Minnesota (1982-1986) and an honorary fellow at the University of Wisconsin at Madison (1992-1993).