Pigments & Dispersions for Energy Curable Inkjet Inks

Mark Ortalano, George Robertson, Stanislav Vilner; Sun Chemical Corporation; Cincinnati, Ohio, USA

Abstract

Surface-treated pigments are described. Surface treatment allows for ease of disperse-ability of pigments into monomers that are commonly utilized in energy-curable inkjet inks. The resulting pigment dispersions have low viscosity and high pigment loading. Inks made from these dispersions have properties of small particle size, high filter rates, low viscosity and high chroma. The surface-treated pigments facilitate excellent stability of ink viscosity and filterability after accelerated oven-aging. Surface treatments have a chemical similarity but are optimized for each pigment. The range covers carbon black, phthalocyanine blue, arylide yellow, nickel azo yellow, and quinacridone magenta.

Overview

The demand for outdoor use of ink-jet printed materials has been increasing. Applications include outdoor wrap, such as: vinyl advertising wrap covering trucks, billboards, posters, and signage. Non-aqueous pigmented inks are developed and can be printed directly on polymeric substrates that are used outdoors without lamination and have great weather resistance.

The requirements for ink-jet inks are quite rigorous, especially regarding particle size distribution, rheological behavior, and colloidal stability. One of the major reasons for such demanding requirements for pigment dispersions is the size of the nozzles of printing heads. The diameter of the nozzle is normally in the range of 30-50 microns, so any type of instability in an ink can pose problems with jetting performance.

The Problem

Energy curable inks have traditionally been difficult to pigments. Typically, a clear ink containing monomers, oligomers and other suitable materials is colored with a pigment dispersion. Pigment dispersions are concentrates of pigment dispersed into monomer. Obtaining high pigment loading in a dispersion has been fraught with difficulty due to high viscosity or viscosity build. Traditional flexographic or offset inks flow is important, but is difficult to achieve with traditional pigments. Certain pigments are more problematic than others in regard to having good rheology. Azo reds (metal salts or naphthols), arylide or diarylide yellows, and quincaridone pigments are particularly difficult to stabilize [1].

Ink jet inks are more demanding in application in that the ink must have a low and stable viscosity, and the ink must be free of oversize particles that can cause nozzle malfunction. Oversize particles can grow over time due to flocculation, but a properly stabilized pigment dispersion will overcome these problems when used to color an inkjet ink. Viscosity stability is key since the printer functions at an optimal viscosity range and instability over time will cause problems.

Pigments Suitable for Ink Jet Application

A range of pigments are used for inkjet ink coloration. Carbon black (PK-7) can vary in structure, particle size, oil absorption, shade and optical density. Phthalocyanine blue (PB-15:3 or PB-15:4) is used as cyan. The molecule is copper phthalocyanine and the pigment is generally cubic. This pigment is very lightfast and is the most commonly used blue pigment. Quinacridone magenta (PR-122, PR-202) or quinacridone violet (PV-19) are common magenta shades. The pigment is generally rod-like and the surfaces possess different energies. For example one crystal face has hydrogen bonding, the other is non-polar and yet another face has medium polarity [2]. This pigment is very difficult to stabilize and is prone to high viscosity, presumably due to the varying surface energies of the surfaces of the crystal. Other pigments, such as rubine red (PR-57:1), rhodamine red (PR-81, PR-169) and naphthol red (PR-269) represent various magenta-shade reds, but do not necessarily possess the proper lightfastness and chemical resistance of the quinacridone pigments. Yellows range from rod-like to needle-like crystals and can be very transparent to very opaque, depending upon particle size and shape. Yellows, such as arylide (PY-74) and diarylide (PY-14), are commonly used in flexographic inks, but do not meet the rigorous lightfastness requirements required for outdoor ink jet inks. Certain benzimadizalone pigments (e.g., PY-151, PY-154) or disazo (PY-155) are suitable, but for very high lightfastness requirements the nickel azo pigment (PY-150) has application for outdoor ink jet application. All of the mentioned yellow pigments are difficult to properly stabilize in energy-curable systems.

Pigment Surface Modification

Energy modification of the pigment surface to promote the formation of effective adsorption layers of polymeric molecules (resins, dispersants, and surfactants) has to be found to be a solution for producing stable pigment dispersions with satisfactory properties. It is not unusual for organic pigments, especially polycyclic pigments, to have a surface with low polarity (lack of functional groups, strong electric charges, active centers) [3]. In many cases, the low polarity may be explained by the morphology of the primary pigment crystals, and intra- and inter-molecular hydrogen bonding [4]. As a result, the adsorption energy for a wide array of polymers and surfactants is low, and may be characterized as a physical adsorption. This type of adsorption is reversible, and it may not provide an efficient barrier to flocculation, due to the desorption process.

There are various methods to facilitate modification of the pigment surface. Some include introduction of functional groups during the course of pigment synthesis, direct reaction on the surface of the pigment and the use of synergists.

The method of introducing functional groups during the course of synthesis of pigments entails the partial replacement of intermediates with analogous intermediates carrying active groups. This technique of chemical modification is well-known for azo [5], phthalocyanine [6] and quinacridone [7].

Direct reaction on the surface of a pigment has been widely practiced as a way to modify surface properties. One of the earliest techniques was a treatment of azo pigments with primary amines, resulting in the formation of azomethine groups (Schiff's bases) [8]. Other reactions have been described as well: sulfonation with sulfur trioxide [9], or sulfur trioxide/pyridine complex [10]; Friedel-Crafts alkylation [11]; azo coupling [12]. The direct reactions on the pigment surface have been especially fruitful for carbon black pigments, due to their highly developed and reactive surface [13, 14].

One of the oldest and popular methods for surface modification is the use of synergists, which are derivatives of organic pigments with a strong affinity for the pigment surface. One of the earliest original studies was carried out with phthalocyanine pigments [15]. As soon as the mechanism of stabilization of the dispersions was understood, the approach was extended successfully for other classes of organic pigments [16]. The synergists could be soluble or insoluble in application media. The soluble compounds are similar to dyes. Less soluble synergists behave more like pigments. The mechanism of surface modification with soluble or partially soluble compounds can be described in terms of adsorption from the liquid phase. The adsorption energy, the thickness, and the structure of the adsorption layers may be determined from the isotherm of adsorption and other experimental data. The mechanism of surface modification with insoluble synergists is not quite clear. It is believed that the synergists make up solid solutions with pigment crystals, or at least partially penetrate and modify their crystal lattice. The insoluble synergists often demonstrate the ability to stabilize pigment

In general, a synergist consists of a moiety of the pigment, one or more functional groups, connecting groups, and other substituting groups. A wide variety of synergists representing various classes of chromophores and functional groups, are described in relevant literature. Some examples of chromophores are phthalocyanines, quinacridones, quinacridonequinones, anthraquinones, perylenes, azo, azomethines, benzimidazolones, perinones, and dioxazines. Functional and connecting groups can include, but are not limited to, sulfonic acids; metal salts of sulfonic acids; salts of sulfonic acid with primary, secondary, tertiary, and quaternary amines; sulfonamides; alkyl amines; carboxylic acids; and amides.

These various techniques of surface treating pigments can offer the pigment manufacturer flexible means for producing high performance pigments and dispersions with improved coloristical, rheological, and stability properties.

Treated Pigments Optimized for Energy-Curable Applications

Surface treatments for pigments to enhance rheological properties are known for use in solvent-based inks for packaging applications [17], publication gravure inks [18] and in energy-curable flexographic printing inks [19].

In the latter patent, energy-curable flexographic printing inks contain a pigment, a rheological additive having the structure P-(U-Y)x, wherein P is the residue of an organic pigment or dye, Y is a polyalkylene oxide moiety, U is a linking moiety covalently bonding Y to P and s is an integer from 1 to 3 [19]. Various pigments were dispersed into monomer and oligomer, and low viscosity millbases were enabled with the surface treatments. Without surface treatments, the dispersions were generally higher in viscosity, lower in gloss and lower in color density. Treated pigments included Black 7, Blue 15:4, Green 7, Orange 16, Red 22 and Yellow 12. The surface treatment for the black & blue are phthalocyanine derivatives, while the Yellow 12 is based upon acetoacetanilide. Carbon black responds well to phthalocyanine-based additives due to the nature of the surface of the black pigment.

The value of these treated pigments is that the dispersion base or ink is allowed to have good monomer acceptance. Ordinarily, non-treated pigments do not allow for smooth monomer reduction. Replacement of an oligomer with a monomer does not necessarily equate with lower viscosity. In fact, the dispersion loses flow and develops a thixotropic rheology when oligomer is replaced with monomer. Some pigments may yield a dispersion with an initial low viscosity. In particular, arylide yellows and azo reds may initially have low rheology immediately after the dispersion is milled; however, after a period of aging the dispersion increases in viscosity. Further reduction with monomer reduce viscosity, but again after a period of aging the dispersion increases in viscosity. Specific surface-treated pigments do not exhibit this behavior. Larger amounts of monomer may be utilized instead of oligomer without sacrificing good flow characteristics. The polyalkylene oxide tail of the surface-treated pigment has great affinity to the monomer phase and enhances the dispersion properties. It inhibits flocculation due to steric hinderance.

Energy-curable ink jet inks typically contain high concentration of monomers, with only minimal amounts of higher molecular weight materials. This is due to the fact that the ink must print at a low viscosity and monomers are used for viscosity reduction, while higher molecular weight materials tend to increase viscosity. Surface-treated pigments of the type described above are well-suited for ink jet ink application.

Experimental

Pigments were dispersed into monomer with the optional use of other proprietary materials by use of a media mill. Mills can be recirculating or discrete pass and utilize ceramic media. A premix was first formed followed by milling until fully dispersed to a fine particle size. The monomer chosen was neopentyl glycol diacrylate, though other monomers can be used. The dispersions were reduced into an ink by use of additional monomer. From the inks were measured filter rates and ink viscosity data. Particle size was measured by a Nanotrac UPA™ instrument, ink viscosity from a Brookfield™ viscometer with a low viscosity adapter, and filter rates through a vacuum filter apparatus (with a 3 micron filter). Oven-aging of the inks was performed at 50C for a period of one month.

Results & Discussion

A surface treatment additive having the structure P-(U-Y)x, wherein P is the residue of an organic pigment or dye, Y is a polyalkylene oxide moiety, and U is a linking moiety covalently bonding Y to P, was used in the case of black and blue with the residue being a phthalocyanine [19]. For the magenta, a sulfonated derivative of quinacridone pigment complexed with an etheramine was utilized [20]. Finally, for the Nickel Yellow 150 pigment a polyalkoxy benzimide was employed as the surface treatment [21].

Solids and viscosity of dispersions are given in the table below. Without the surface treatment the dispersion viscosities are >10000 cps, and exhibit poor flow and are difficult to dispense. Generally, high pigment loadings with low viscosities are enabled by surface treating the pigment via this technology.

Dispersion Properties

Color	%Pigment	Viscosity (cps)	Particle Size d50 (nm)
Black 7	26.5	730	140
Blue 15:4	25.0	7400	228
Red 122	23.0	753	258
Yellow 150	16.0	1020	217

Ink viscosity is measured at approximately 3.0% pigment loading. Stability after oven-aging at 50C is presented in the table below. All viscosities are stable within the capability of the measurement system. Additionally, all viscosities are in the range of that for ink jet printing. Lack of change in viscosity is indicative of excellent flocculation resistance. Without the use of the surface treatment, the viscosity rises significantly, particularly with the magenta and yellow. The untreated magenta had an ink viscosity of 50 cps, which is far higher than that required for printing in most printheads.

Ink Viscosity Data & Ink Filter Rates

Color	Initial Viscosity (cps)	Viscosity After Oven-Aging (cps)	Initial Filter Rate (sec.)	Filter Rate After Oven-Aging
Black 7	7.02	6.57	55	58
Blue 15:4	8.60	9.00	58	65
Red 122	8.34	7.80	62	54
Yellow 150	7.56	7.71	49	54

Filter rates were timed as to how long 150 grams passed through a 3 micron filter. Each dispersion filtered at a somewhat different rate, depending upon the color. After oven-aging at 50C for four weeks, none of the dispersions exhibited any change within the capability of the measurement system. This is indicative of the excellent stabilization achieved with the surface treatment. Poorer stability is exhibited without the treatment, particularly with the magenta and yellow. The initial filter rate of untreated magenta was 66 seconds, but after four week oven-aging this increased to 196 seconds.

Overall, the surface treated pigments have great utility in facilitating the coloration of energy-curable ink jet inks. Excellent stability of inks in regard to filter-ability and viscosity is found, and this is due to reduced potential for flocculation. Dispersions are low in viscosity and are well-developed in color hue and chroma. The surface treatments of magenta and yellow are particularly desirable since these colors are of great value in the ink jet market.

References

[1] M. Ortalano, "Advancements in Pigment Dispersion", NPIRI Conference, St. Charles, IL, October 2004.
[2] M. Ortalano, "Pigment Dispersions for Toners and Ink Jet Systems", IMI Conference, Orlando, FL, February 2007.
[3] R. Sappok, J. Oil Col. Chem. Assoc., 61 (1978), 299-308.
[4] W. Herbst, K. Hunger, Industrial Organic Pigments, VCH, 1997).
[5] R. Schwartz, US Patent 5,021,090.
[6] V. Wainmayr, US Patent 3,006,921.
[7] V. Mitina, US Patent 6,284,890.
[8] R. Schwartz, US Patent 4,468,255.
[9] M. Nakamura, US Patent 6,821,334.
[10] T. Uemura, US Patent 5,928,419.
[11] J. Watson, US Patent 3,043,708.
[12] P. Bugnon, US Patent 6,896,726.
[13] A. Karl, US Patent 6,780,389.
[14] A-G. Yeh, US Patent 6,852,156.
[15] W. Black, Kolloid-Zeitschrift and Zeitschrift für Polymere, Bd.213, Heft 1-2, (1966), 150-156.
[16] J. Schroeder, Progress in Organic Coatings, 16(1988), 3-17.
[17] G. Robertson, US Patent 6,471,764.
[18] R. Schwartz, US Patent 5,062,894.
[19] M. Laksin, US Patent 6,284,816.
[20] S. Vilner, Patent Filed.
[21] T. Romanova, Patent Filed.

Author Biography

Mark Ortalano is Manager of Dispersions Technology at Performance Pigments of Sun Chemical Corporation. He has been with Sun Chemical since 1992, and is a Certified DfSS Six Sigma Black Belt. His major responsibility at Sun is to develop innovative color technologies for various markets, particularly digital printing. Mark has a B.S. in Chemistry from Louisiana State University, a M.S. in Physical Chemistry from New York University and a Ph.D. in Chemistry from Louisiana State University. He did a postdoctoral in laser physics at Texas Tech University.