Novel Hybrid Pigment/Dye Dispersions

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Abstract

Novel aqueous pigment dispersions containing only dye as the pigment stabilizer are discussed. These dispersions contain well-dispersed and stable pigment, dye and water. The dyes employed are of high purity and are commonly utilized as ink jet dye colorants. Optionally, humectants such as glycols or glycerines may be added, as well as amines and biocides.

The resultant dispersions have very fine particle sizes and high surface tensions, and have a low tendency to flocculate when reduced back in prototypic ink jet ink formulas. Additionally, low and stable viscosity ink profiles are obtained when using these dispersions to color prototypic ink jet inks.

Development work focused on black dispersions. However, process colors are discussed, as well. These dispersions allow the ink to have hybrid properties of a pigment and dye, without the limitations imposed by the inclusion of traditional dispersants, such as surfactants or polymers.

Introduction

Aqueous ink jet inks are colored with either pigments or dyes. Dyes are commonly used as colorants for ink jet inks, but their use has limitations. For example, dyes do not have a high degree of resistance to light, and therefore can fade in the presence of visible and/or UV radiation. Of course, some dyes have very good lightfastness, but others have very poor fade resistance. The dyes commonly used in ink jet printing generally have functionality to render them water-soluble. This functionality has the negative impact of contributing to water bleed problems in the printed ink. Additionally, highlighting an ink jet ink film with a marker typically causes a great deal of ink bleed. Even with the negative aspects that dyes impart to inks, dyes have very common usage in ink jet printers, particularly in the SOHO market. Their wide usage can be attributed to their very wide color gamut and their very high degree of stability in common ink systems. That is, dye-based inks do not readily clog nozzles and exhibit excellent maintenance in both thermal and piezo print heads

Pigmented ink jet inks are used mainly in areas that require excellent lightfastness. Large format signs and billboards are printed with pigmented ink jet inks. Other applications include markets that have traditionally used pigmented inks, such as rotary screen, gravure and flexographic inks. These markets include, but are not limited to the following: textiles, wall coverings, floor coverings, packaging and labels. Pigmented inks can exhibit excellent lightfastness, dependent upon the pigment chosen. Pigments are generally very resistant to water, solvents and heat. Unlike dyes, pigments have to be dispersed into water by additives, such as resins and/or surfactants. Resins can have the negative impact of degrading under heat and forming water-insoluble fragments on the printhead. Surfactants can lower the surface tension to an undesirable level, thereby affecting dot gain.

It is the purpose of this paper to describe a novel pigment dispersion that can be used to color aqueous ink jet inks. This dispersion employs commonly used ink jet grade dyes to disperse pigment, thereby eliminating any negative attributes of conventional resins or surfactants that would ordinarily be used as dispersants. The new hybrid colorants enable the use of pigments without the negative impact of traditional dispersants, while taking advantage of the positive attributes of dyes, such as high optical density, wide color gamut and high thermal stability.

Traditional Pigment Dispersions

Water-based pigment dispersions contain pigment fully dispersed to the primary particle (or crystal) size. This can be accomplished by various milling techniques, one of which being media milling. Basically, dry pigment or presscake is in a highly aggregated state. That is, dry pigment is composed of aggregates of primary particles. The milling process involves de-aggregation of the pigment aggregates down to their primary particle size (generally 0.05 – 0.25 microns). Because pigments are generally very hydrophobic, dispersants are required for pigment stabilization in water. That is, pigments will flocculate in water unless properly stabilized by a surfactant and/or a resin that has certain properties. One very important property is that the dispersant has a hydrophobic portion that has affinity for the pigment surface, and that the dispersant has hydrophilic character to enable a coupling between the pigment and the water phase. Common surfactants are alkyl phenol ethoxylates, where the alkyl phenol portion is the hydrophobe and the ethoxylate is the hydrophile. Common resins used as dispersants are alkali soluble styrene acrylic resins, that contain hydrophobic pockets of styrene (and certain acrylates) and hydrophilic components of amine solubilized acrylic acid. Block copolymers are also used as dispersants, as well as anionic and cationic surfactants. There are other commercially available pigment dispersants, some of which are described in reference 1.

These pigment dispersions are then used as the color component for many different water-based products, such as flexographic and gravure inks, rotary screen inks, paints and coatings, textile colors and pulp paper colorants. Common pigments chosen are Carbon Black (C.I. Pigment Black 7), Phthalocyanine Blue (C.I. Pigment Blue 15:3), Quinacridone Magenta (C.I. Pigment Red 122), B/S Naphthol Red (C.I. Pigment Red 238), Diarylide (AAOT) Yellow (C.I. Pigment Yellow 14) and Monoarylide Yellow (C.I. Pigment Yellow 74). A more comprehensive listing of pigments may be found in reference 2.

Ink jet inks are colored with pigment dispersions, as well, but can suffer the negative aspects of the dispersant chosen. Surfactants lower surface tension of the ink, thereby affecting dot gain. Resins can break into water-insoluble fragments on the printhead, thereby causing maintenance problems with the printhead. Also, resins can lose water-solubility by the amine flashing off with heat causing pigment flocculation and viscosity changes in the ink. However, pigments do have definite advantages, and depending upon proper pigment selection, pigmented ink jet inks can exhibit excellent lightfastness and water-fastness. This high level of fastness is due, in part, to the pigment being a primary particle (or crystal) of discrete sub-micron particle size. Each primary particle or crystal is composed of an extremely large number of pigment molecules, each of which is insoluble in water. Because the color is a particle rather than a soluble molecule, higher performance properties are obtained.

Dye-Based Systems

Dye-based ink jet inks are very commonly used in ink jet printing due to their excellent stability and maintenance. They also have a very wide color gamut. However, dyes must be chosen carefully, and must have low conductivity and high purity to ensure good performance. Dyes used in ink jet printing include, but are not limited to the following: Reactive Black 31, Direct Black 168, Direct Blue 199, Direct Blue 86, Acid Blue 9, Acid Red 51, Acid Red 52, Reactive Red 180, Reactive Yellow 37 and Direct Yellow 132. See reference 3 for additional details. Dyes are different from pigments in that they are soluble in water, and dissolve to the molecular (or molecular cluster) state. The aforementioned dyes are water-soluble due to certain functionality on the dye, such as sulfonation. This water-solubility allows for excellent performance and maintenance, but can render the printed ink water-sensitive. Additionally, the lightfastness of these dyes are not extremely high. The reduced fastness properties of dyes relative to pigments is partly due to the relative size differences between dyes and pigments. Dye molecules are more susceptible to radiation and chemicals than pigment primary particles that contain an extremely high number of molecules packed together in a crystal lattice.

Dye/Pigment Dispersions

The following describes pigment dispersions utilizing dye as the sole dispersant. That is, the dispersion contains fully dispersed pigment and dye as the dispersing agent. Water is the carrier. The ability of certain dyes to disperse pigment is presumably explained by taking into consideration select structural similarities between certain dyes and certain traditional surfactants. For example, some ink jet dyes are sulfonated (giving hydrophilic components), and they also contain aromatic or heterocyclic hydrophobic components. This is similar to the way certain dispersants behave, such as the naphthalene sulfonates. Based upon the high performance of these dyes in ink jet, it is possible to create a hybrid dye/pigment dispersion that will give good performance in ink jet printing.

Black Dye/Pigment Dispersions

Carbon black pigment (C.I. Pigment Black 7) is a common pigment used in printing inks. It is very jet, but the jetness (or optical density) depends upon the grade of pigment. Numerous grades of carbon black pigment are available and they differ by primary particle size and oil absorption.

Carbon black pigment was dispersed by use of two common dyes used in ink jet, Direct Black 168 and Reactive Black 31. The dispersion was facilitated by media-milling a premix of high purity black dye solution and carbon black pigment. Table I below describes four dispersions indicating the amount of active dye and pigment. The remainder of each formula is composed of highly pure water. Additionally, a comparative example is given indicating a conventional surfactant stabilized-commercial carbon black dispersion.

Table I. Black Dispersions

Black Dispersion A	14.0% Cabot Regal™ 330 7.0% Direct Black 168
Black Dispersion B	20.0% Cabot Regal™ 330 10.0% Reactive Black 31
Black Dispersion C	20.0% Columbian Raven™ 5000 Ultra 10.0% Reactive Black 31
Black Dispersion D	20.0% Cabot Regal™ 350R 10.0% Reactive Black 31
Comparative Example	22.0% Cabot Regal™ 330 11.0% Surfactant Blend 5.0% PEG

Particle size distributions of the dispersions were measured by using a Honeywell Microtrac™ UPA 150 particle size analyzer. The mean value along with the 10th and 90th percentiles are given in nanometers for the above dispersions. The data is tabulated below:

Table II. Particle Size Data of Black Dispersions

Black Dispersion A	Mean: 111.4 nm 10%: 54.0 nm 90%: 179.1 nm
Black Dispersion B	Mean: 108.5 nm 10%: 60.8 nm 90% 159.1 nm
Black Dispersion C	Mean: 84.0 nm 10%: 29.4 nm 90%: 187.4 nm
Black Dispersion D	Mean: 183.0 nm 10%: 116.5 nm 90%: 262.1 nm
Comparative Example	Mean: 158.5 nm 10%: 95.6 nm 90%: 228.3 nm

These dispersions were reduced into prototypic ink jet ink formulas, where particle size data was measured initially and after oven aging (at 120F) for 2 weeks and for 6 weeks. The diluents chosen were distilled water, and combinations of 1/1 water/propylene glycol and 1/1 water/PEG-400. In each ink, 15% dispersion was blended with 85% diluent. The (mean) particle size stability data for Black Dispersion B in each prototypic ink is tabulated below:

Table III. Particle Size Stability Data of Black Dispersion B in Prototypic Inks

Water	Initial: 108.5 nm 2 Weeks: 108.9 nm 6 Weeks: 108.6 nm
Water/Propylene Glycol	Initial: 117.0 nm 2 Weeks: 133.8 nm 6 Weeks: 134.6 nm
Water/PEG-400	Initial: 98.7 nm 2 Weeks: 164.3 nm 6 Weeks: 209.1 nm

Optical density was measured after applying an ink film onto various media, accounting for the background of the media. The absolute values of the optical densities depended upon the ink formulation used. However, Black Dispersion A and Black Dispersion B on average had 40% higher optical density than the dispersion of the comparative example.

Surface tension was measured on the various dispersions in the prototypic ink systems. In the case of Black Dispersion B letback into water, a surface tension of 69.9 dynes was measured.

These black dye/pigment dispersions exhibit low particle sizes and narrow particle size distributions. These particle sizes are stable in prototypic ink jet ink formulas over oven aging up to 6 weeks at 120F. High surface tensions are obtained, as well as high optical densities. Prototypic ink jet inks exhibit low and stable viscosities when utilizing these dispersions.

Colored Dye/Pigment Dispersions

Colored pigments were dispersed with select dyes that have common usage in ink jet printing. A few of these dispersions are described below, where the amount of pigment and dye are listed on a solids basis. Ultrapure water composes the remainder.

Table IV. Colored Dispersions

Blue	20.0% C.I. Pigment Blue 15:3 10.0% Acid Blue 9 dye
Magenta	26.0% C.I. Pigment Red 122 13.0% Acid Red 51 dye
Yellow	20.0% C.I. Pigment Yellow 14 10.0% Acid Yellow 194

The particle size data and surface tension for the above dispersions are tabulated below, where the mean value, the 10th percentile and the 90th percentile are given.

Table V. Particle Size Date of Colored Dye/Pigment Dispersions

Blue	Mean: 199.6 nm 10%: 69.9 nm 90%: 348.5 nm
Magenta	Mean: 172.6 nm 10%: 73.0 nm 90%: 265.7 nm
Yellow	Mean: 120.6 nm 10%: 52.1 nm 90%: 206.7 nm

The above particle size data is similar to that obtained from conventional resin-stabilized dispersions. Additionally, the color is much brighter for the above magenta than that obtained from a traditional surfactant or resin stabilized pigment dispersion. This is due to the high color gamut of the Rhodamine dye. Overall, the dye enhances the color of the pigment dispersion, and the composite system has color gamut between that of a pigment and that of a dye.

All of the above dispersions have surface tensions higher than their traditional resin or surfactant stabilized counterparts.

Additives

Additives can be used to give the dye/pigment dispersions certain functional properties other than pigment stability. For example, humectants (such as propylene glycol, glycerine, PEG) can be added to impart freeze/thaw stability. Biocides can be added to retard bacteria, mold and yeast growth. Defoamers can be used to reduce foam formation. Amines, such as ammonia or MEA, can be used to modify pH. Acids can be used to reduce pH. These additives do not contribute to particle size reduction or stabilization. They can be used simply to impart the above-mentioned properties to the dispersion.

Conclusion

Dispersing pigment with dye is very unique and eliminates the need for surfactants or resins to facilitate a fine particle size pigment dispersion. The pigment dispersions described in this paper have the following attributes: (a) low particle sizes and a narrow particle size distributions; (b) particle sizes that are stable to oven-aging; (c) no settling or separation; (d) high surface tensions; (e) lowers tendency to foam; (f) avoids the negative impact on color that can be caused by the use of certain surfactants; (g) sustains or increases color gamut; and (h) exhibits high optical density with respect to black.

These dispersions can have efficacy in ink jet applications where dyes are conventionally used, where the use of lightfast and chemical resistant pigments can improve upon the overall performance of the dye-based ink. The dyes can improve the color gamut of the pigment set, as well as boost the optical density of the overall black ink. Higher surface tensions enable greater leeway in the ink formulation.

In summary, these dispersions represent unique hybrid colorants for ink jet ink systems, with properties common to both pigments and dyes.

References

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Biography

Mark Ortalano is Research Manager at the Dispersions Division of Sun Chemical Corporation. He has been with Sun Chemical since 1992. His major responsibility at Sun is to develop innovative color technology for various markets, particularly non-impact printing and colored waxes. Mark has 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.