

Organic, Cationic, Sub-Micron Particles for Ink Jet Paper Coatings

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Abstract

The novel cationic polyfunctional oligomer (DA-C) and novel cationic sub-micron organic particle (COP) have been developed. DA-C is placed in the hydrophilic polyacrylates and COP is placed in the crosslinked polymer particles. COP is synthesized by using DA-C and co-monomers with non-aqueous dispersion polymerization or reverse suspension polymerization. COP is designed to have high absorptivity and fixing ability of aqueous ink jet ink. The absorptivity , swelling, and dye-fixing ability of COP were measured. These properties were kept up in experimental COP paper. The advantages and future direction of this technologies are discussed.

Introduction

Print quality, fastness, and permanence of ink jet prints have more and more become important. The material selections of colorant and paper are major subjects of it. Most of the prints we read on daily life may be thrown away after short stock periods. But the stability of these prints naturally gives us a sure reliability to the printing system. To get such a reliability also on ink jet printing is focusing subjects in a R/D work. To enhance a fastness and permanence of the print of aqueous ink jet system are still the first key factor. The typical ink jet coating is composed of precipitated and/or fumed silica, binder, and additives. The finely milled silicas have a good sorption capacity and speed by their high surface area. The silica based coating has become the standard way for the ink jet paper coating. The silica based coating layer is usually strengthened by adding a mordant to improve a water/moisture resistance. The another typical inorganic pigment is Al_2O_3. Al_2O_3 has a positive ζ surface ionic potential within a wide range of pH in an aqueous solution.

Al_2O_3 interacts attractively with anionic, negative charged dyes and pigments and layers made from it show better water fastness than silica based coatings. The disadvantage of the such inorganic pigments as silica and Al_2O_3 coating is a stiffness, fading effect on azo dyes in air, imperfect moisture resistance, and narrow flexibility on base sheet selection.

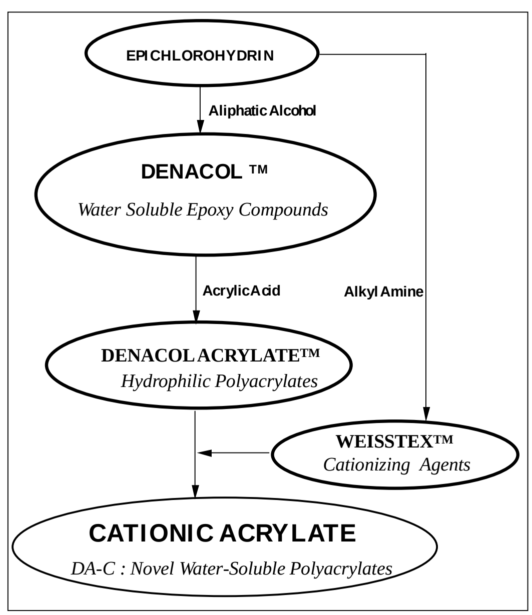
In this paper, we explain the development of the novel, cationic, sub-micron particles for ink jet paper coatings. The organic particles may overcome some above disadvantages in addition to the water fastness. On developing the organic particles, we focused particularly to balance the absorptivity and colorant fixing. The size and void volume of the particle has a great influence to an absorptivity and transparency of the layer. The first step of this development is to produce the sub-micron sized particles of strongly hydrophilic by cation, which absorb inks by swelling and fix the colorants.

Experimental

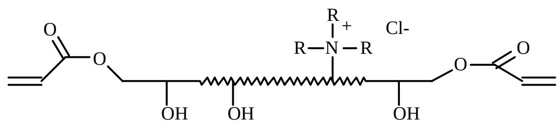
Cationic Oligomers (DA-C)

DA-Cs were designed to satisfy the requirements from the non-aqueous polymerization of COP. DA-Cs are the reaction products of the polyepoxide of the hydrophilic polyols (they are DENACOL™ from Nagase Chemicals Ltd.), cationizing agent and acrylic acid.

EPICHLOROHYDRIN Derivatives and CATIONIC ACRYLATES

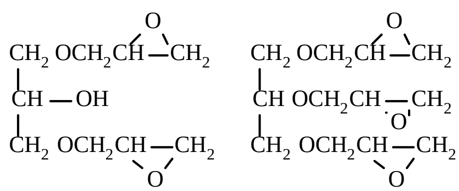


The principal synthetic root of cationic acrylate, DA-C, is shown in above diagram. The schematic formula of DA-C is as follows.



The skeleton of the DA-C is polyglycidyl ether of polyol, which is DENACOL™ . Typical raw materials for DA-C are shown in Figure1.

DENACOL™EX-314 : glycerol polyglycidyl ether



DENACOL™EX-512 : polyglycerol polyglycidyl ether

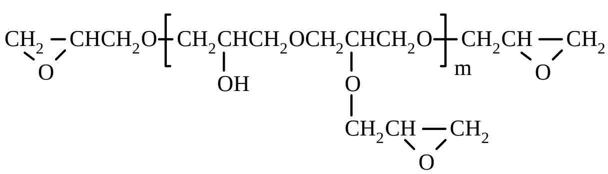


Figure 1. DENACOL™ as a raw materials for DA-C :

In DA-C molecule at least one cationic group and two or more vinyl polymerizing group are attached. DA-C molecules of this category are hygroscopic, cross linkable, and highly soluble in water. DA-C can be used as a UV curing resin also, cured film of which is colored strongly by dyes and pigments for ink jet. Once the film is colored, it wasn't decolorized under even long immersion in water. The film made from DA-C swells also by absorbing water. These properties are suitable for the ink jet paper coating and synthesis of coating polymers in their reactivity, absorbency and fixing ability. DA-C can also be used as cross-linking agents for water soluble high polymer, cationizing agent, and raw materials for synthesis of sub-micron organic particle.

Synthesis of Cationic Organic Particle (COP)

The COP is cross linked polymer particle from hydrophilic monomers by non-aqueous dispersion polymerization method. COPs are synthesized with DA-C, hydrophilic monomer, oil soluble soap, organic solvent, and initiator. COP are synthesized by non-aqueous dispersion polymerization or reverse suspension polymerization. The particles can be supplied in as-grown, non-aqueous dispersion form or aqueous dispersion form, or dried powder form. If it is necessary to crush to smaller particles, the rough powder can be milled under freezed state. With these procedure hydrophilic, cross-linked particles having the particle size diameter of from 100 to 1000nm are produced. The particle size depends on the synthetic way. The key parameter to control the water absorptivity of COP is amount of the crosslinking monomer in the polymer particle, which is illustrated in Figure 2. The hardness of the particle is controlled by choosing the co-monomer selected from the group of methacrylate monomers and other hydrophilic monomers. Typical shape of the COP is shown in Figure 4(a) and 4(b).

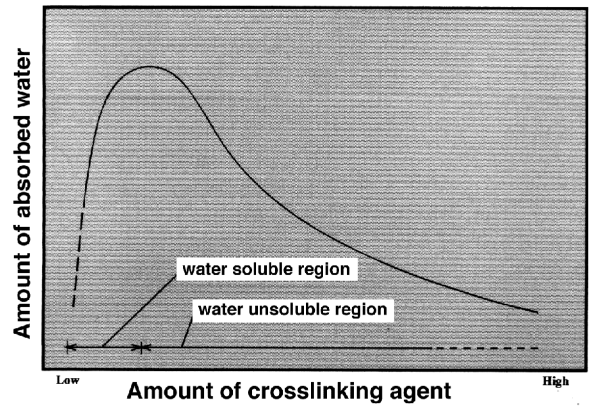


Figure 2. Relation of amount of absorbed water vs. amount of crosslinking agent on polymerization of COP

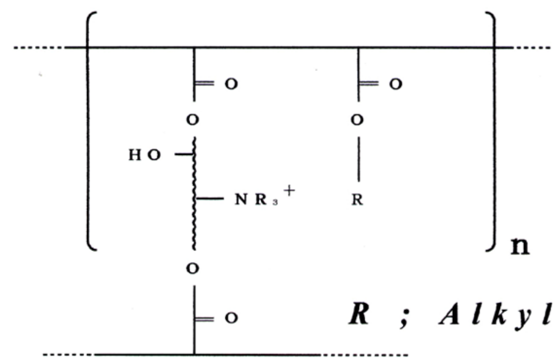


Figure 3. Chemical structure of COP

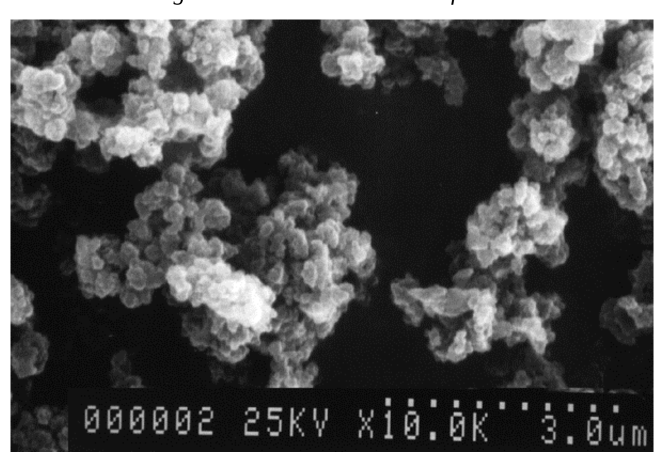


Figure 4(a). COP prepared by non-aqueous dispersion polymerization. Primary mean particle size : 300nm.

The COP are now placed in the products line up as **RS series** in SOKEN Chemicals & Engineering Co.

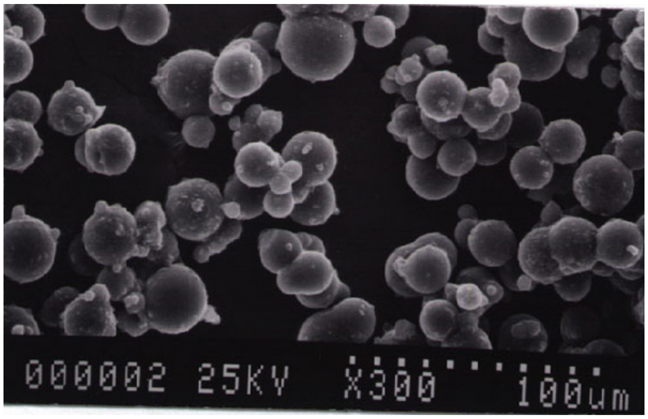


Figure 4(b). COP prepared by reverse suspension polymerization Primary mean particle size : 1500nm.

Chemical Properties of COP

COP is hydrophilic, polycation particle charged by many number of quartenary ammonium substituents both on the surface of and inner side of the particle. The polarity of COP resembles the Al_2O_3 particle, but COP can swell by water.

Swelling

Swelling of spherical COP by magenta dye ink is shown in Figure 5. The swelled COP became large a little. The crosslinking restricts more expansion. The size was reversible by warming but adsorption of dye was irreversible.

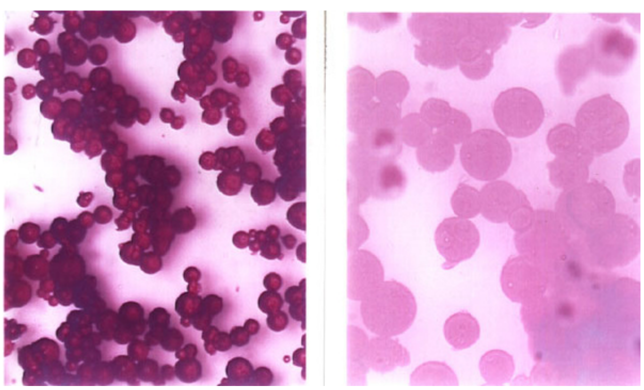


Figure 5. Swelling of spherical COP by aqueous ink; left : before swelling; right : after absorbing magenta ink

Dye Adsorption

The COP is strongly colored with dyes and pigments likewise an aluminum oxide. The silica does not be colored to such an extent as COP and aluminum oxide. The irreversible adsorption of ink jet magenta dye to COP is shown in Figure 6; Desorption test. In the case of neutral, non-cationized particle, dyes adsorbed in the particle easily dissolved into water, on the other hand, the dyes adsorbed in COP particle didn't any more dissolve into water. The characteristics of COP is these strong irreversibility, which was given essentially by adopting the DA-C monomer as a cationizing agent.

Figure 6. Desorption test from COP; left:neutral (non cationized); right : COP (cationized)

Sorption of Ink

The sorption speed of ink in COP was measured with Dynamic Wetting Apparatus. The increments of weight of dried particles were measured as an adhesive force with the ink into the dried particles. Silica and aluminum oxide were tested for the comparison. Figure 7 shows the relative absorption of three dry particles.

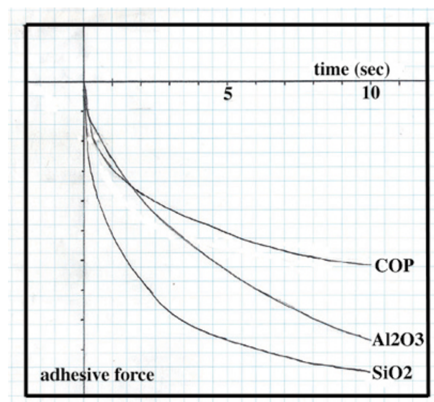


Figure 7. Wetting curve of COP with ink mean particle size of test samples; COP:300nm, Al_2O_3:100/10nm, SiO_2:700/15nm (aggregate/primary)

In an inorganic particles there aren't any swelling, then absorption continues for long time. On the other hand in case of COP the rate became slow gradually.

Table 1. The Amount of Absorbed Water in Unit Weight of Particle

particle	absorbed water (g/g)
aluminum oxide	2.1
fumed silica	1.9
precipitated silica	4.6
COP	3.0

In Table 1 the amount of absorbed water in unit weight of particle is listed. The total amount of ink absorbed under saturation is same level within the tested samples. The curve means that swelling reduces the continuous sorption into COP particle agglomeration. It is needless to say that the initial sorption rate is important in ink jet printing. To increase the volume and speed of sorption in COP, it will be better to make COP smaller and higher void volume.

The size of the COP can be made smaller by optimizing the polymerization condition. The transparency of the layer depends also on the size of the particle. Transparent layer with COP could be attained by using the particles having the diameter of smaller than 300nm. These observations denote the COP can basically be used for the pigments in an ink jet paper coatings.

Ink Jet Receiving Sheet

The experimental COP papers were made by using the polyurethane dispersion as the binder material. The print quality, rate of absorption, water fastness, and preservation properties (light fastness, yellow stain) were tested for these papers. Figure 8 shows the absorption speed measured with bristow's apparatus.

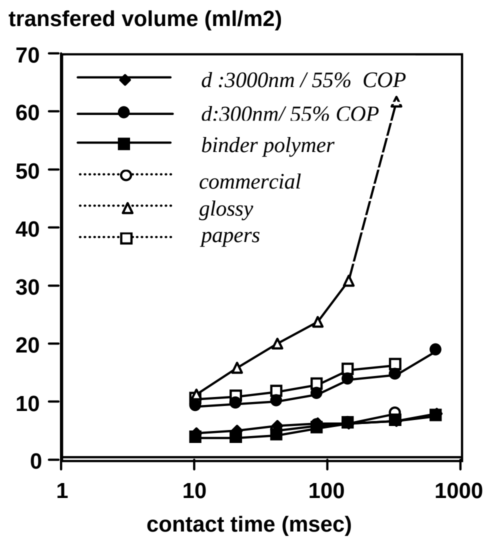


Figure 8. Absorption rate of COP paper

From Figure 8 the particle size effect is apparent in absorption rate, i.e., COP having sub-micron diameter is better to give higher absorption rate. The rate of COP paper is close to two commercial glossy papers whose predominant mechanism is swelling absorption.

Water Fastness

The water fastness of experimental COP paper is better compared to commercial glossy papers as shown in Figure 9.

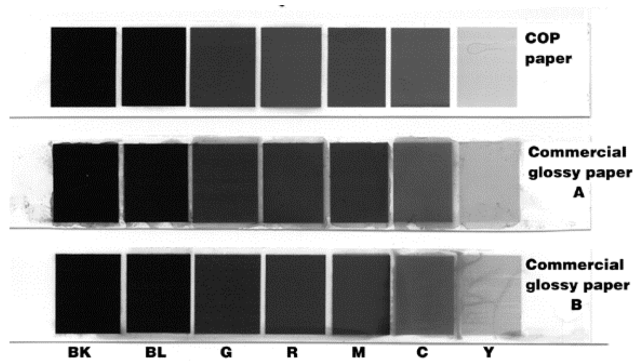


Figure 9. Water-Fastness Test; The test samples were immersed in water for 1 min.

On testing water-fastness in Figure 9, the inks contained the first generation ink jet dyes, test patterns were primary CMYK and secondary RGB colors. The experimental COP paper showed the higher water-fastness especially after the long term immersion in water.

Advantages and Future of COP

Particle Size Flexibility

COP will be supplied in dry powder form or non-aqueous dispersed form, whose mean particle size can be controlled from 100 to 1000 nm. The particle size can be selected from the practical usage.

Transparency

The coating layer made mainly from COP is transparent when the mean particle size is smaller than 300nm.

Image Stability

The non-aqueous system makes it possible to let the stabilizers into a coating. The dye stabilizers to prevent a photochemical and oxidative break down are usually non-aqueous compounds. To introduce such a material in paper coating, COP dispersion is quite suitable. The organic particle by itself is favorable also than inorganic ones to reduce the catalytic fading of dyes and yellow stain of the paper.

Image Quality

Because of the minimum scattering of light from the pure organic particulated layer, the image quality becomes better feeling.

Manufacturing of Paper

The non-aqueous system will increase the coating speed.

The production cost of ink jet paper depends greatly on coating speed. COP will be useful for a cost reduction program.

Conclusion

The cationic polyfunctional oligomer, DA-C, and the cationic sub-micron,organic particle, COP, for ink jet paper are developed. These materials will be useful to produce a paper to have a low cost and better quality, and satisfactory fastness properties.

Reference

general literature for polymerization of polymer particles:
R. Arshady *Colloid Polymer Science* **270**, 717-732 (1992)