Gas Fastness of Dye Based Ink

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Abstract

We discussed some kinds of additives for inkjet ink to improve ozone fastness of a print image. Test patches were printed by an inkjet printer using water base ink containing the additive, water soluble dye, glycerol, and some penetrants which are inactive to ozone. The ozone concentration of exposure test was 26ppm. We quantified hue change between initial print and the one exposed by ozone. First of all, some additives such as benzotriazole and amine, which are known to be effective on improving ozone fastness, and amino acid, which is known to improve dark stability of images, are examined for Cu phthalocyanine dye. We found that amino acid type compounds were more effective on ozone fastness. Next, we examined carboxylate salts and a quaternary ammonium compound to understand the effect of carboxylic group and amino group on ozone fastness. After the examination on many kinds of amine salts of carboxylic acid, the amine salt of low pKa carboxylic acid was found effective on ozone fastness. The mechanism of low pKa carboxylic acid was supposed that when the amine had a counter ion of low pKa acid, it could transfer the lone pair electron to ozone molecule easily. We examined the same additives for azoic dye, and found that the amine salts of carboxylic acid were effective on ozone fastness.

Introduction

In recent years, inkjet printers are able to make a high quality image with affordable price. So inkjet printings have become popular in various fields such as office, personal, and professional use. While inkjet printers are used for various purposes, more stable images have been required. The print images of inkjet printers, especially made with dye-based inks, are said to fade easily in outdoor and indoor environment. It is pointed out that the indoor fading was caused by ozone gas while the outdoor fading was caused by light and ozone gas.

Matsui et al. has been discussed about the decomposition of colorants by ozone gas and categorized its reaction into following five classes[1];

- 1,3-Dipole Addition,
- Electrophilic Attack,
- Nucleophilic Attack
- 1,3-Insertion
- Electron Transfer

Ozone can decompose many kinds of chemicals and actually colorant manufacturer uses ozone for processing of liquid wastes.

A lot of ways to improve ozone fading of print images have been discussed; the use of pigment instead of dye as a colorant, approach from media, and so on. Use of pigment as a colorant is powerful method to improve gas fastness of images,[2] but it still has some limitation on the color reproduction. Approaches from media, such as special coated papers, were also reported[3], but the dependence on media would not be proper answer for various users. Now we discuss about additives for inkjet ink to improve ozone fastness with conventional dyes and plain paper.

Previously some kinds of agents were proposed as anti-ozonant. Matsui et al reported that hindered phenol, bisphenol, and aromatic amine were effective as antiozonant, and aromatic amine was most effective.[4] G.Astorino et al reported that ethylenediurea allows plant to avoid the oxidative stress.[5] C.Z.Qi et al proposed protection mechanisms of p-phenylenediamine-type antiozonants.[6]

In this study, we examined various antioxidant agents such as benzotriazole and amines, which are generally said to be good antioxidant, and amine salts of carboxylic acid. Amino acids, which were reported effective for dark image stability from T. Tanuma[7] and H. Takimoto[8] et al, were also examined.

Experiment

Methodology

As the ozone generator, HTVG-1 (commercialized from SILVER SEIKO Co.) was used. A small print sample was put into a glass chamber, which was linked with ozone generator by Teflon tube, and exposed for designed time under 25°C, 50%RH, dark condition. The ozone concentration was 26ppm measured by quantifying iodine produced in blowing ozone into potassium iodide solution by sodium thiosulfate.

The test ink contained 4% of dye, 10% of glycerol, 10% of triethyleneglycolmonobutylether, 1% of nonionic surfactant, an additive of 10 times molar quantity of dye, and the balance of deionized water. Print samples were made by PM-760 (Epson corp.) with the plain paper (Canon OFFICE A4 80 gsm) and used for the ozone test after dried for overnight.

The change of color after the ozone fading test was measured by spectro color meter SE2000 (Nihon Denshoku

Co.) and expressed by Δ E*ab in CIE1976L*a*b* color space.

Materials

In this study, Cu phthalocyanine dye (C.I. Direct Blue 199) and azoic dye (C.I. Direct yellow 132) were used. As mentioned above, generally speaking, azoic dyes are likely to be attacked by ozone[1]. Phthalocyanine type compounds are known to be stable to light. But print images of Cu phthalocyanine dye tend to change color to be greenish when it is exposed to ozone gas. Therefore it is valuable to find how the dyes can be protected from ozone gas.

As additives, four kinds of chemicals were examined. First are antioxidants, such as water-soluble benzotriazole (commercial name of BT-GL from JOHOKU CHEMICAL CO., LTD.). Second are amine derivatives, such as p-phenylenediamine, aniline, and 2-aminoethanol. Third are amine salts of carboxylic acid made by above mentioned amine and several kinds of acids, such as aliphatic carbonic acid (n-hexanoic acid as monoacid, tartaric acid, and malonic acid as polyacid), aromatic carbonic acid (benzoic acid and phthalic acid). Fourth are amino acids, such as 6-amino-n-capronic acid and trimethylglycine, which has no lone pair electron at nitrogen site in amino group.

Results and Discussions

First, the effect of several kinds of antioxidants, amines, amine salts of carboxylic acid, and amino acid were studied by adding into the phthalocyanine dye based ink. Figure 1 showed the hue changes versus the ozone exposure time.

Amines, which were reported to be effective for stabilization in ozone gas environment,[4,6] and antioxidants showed little effect in this study. The reason of this difference could not be understood well. Especially, p-phenylenediamine showed serious hue change from the beginning of ozone exposure. On the contrary, 2-aminoethanol salt of benzoic acid showed good ozone-fast improvement, and 6-amino-n-capronic acid was also effective in shorter exposure time.

In the early stage of ozone exposure, 6-amino-n-capronic acid retarded color changing well. But after a long-time exposure, the color changing was the most serious of these 5 chemicals. This result showed the permissible ozone volume of amino acid was less than that of carboxylic acid salt of amine. If the dose limitation did not exist for an ink additive, in case of the usage as a media component e.g., amino acid would be the most effective chemical to improve ozone fastness.

From the results of the amino acid and the amine salt of carboxylic acid, if amines were together with acid, amines were supposed to make ozone inactive effectively. The function of acids of this reaction was not clearly understood, but the electrophilicity of carboxyl group could trap ozone molecule and make support the inactivation as a co-catalyst.

To understand the effective state of amines, amine salts of carboxylic acid and quaternary amino acid were studied (Figure 2).

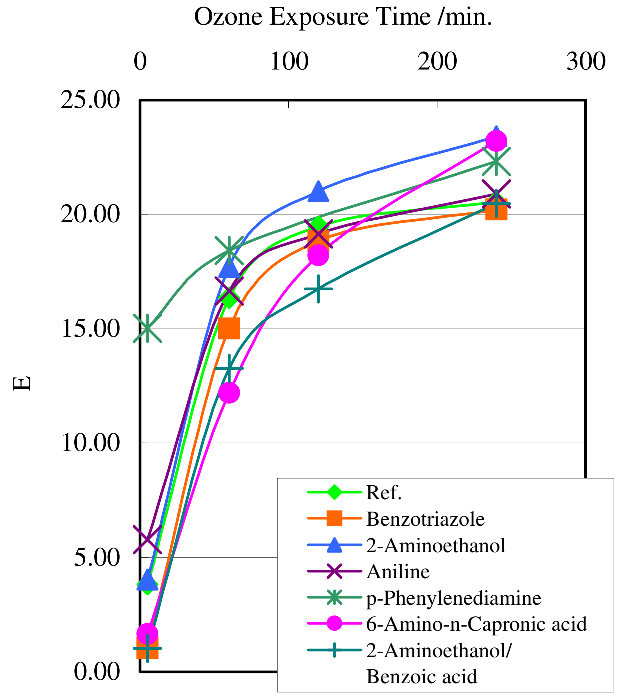

Figure 1. Ozone fastness of Print Images with antioxidants and an amino acid.

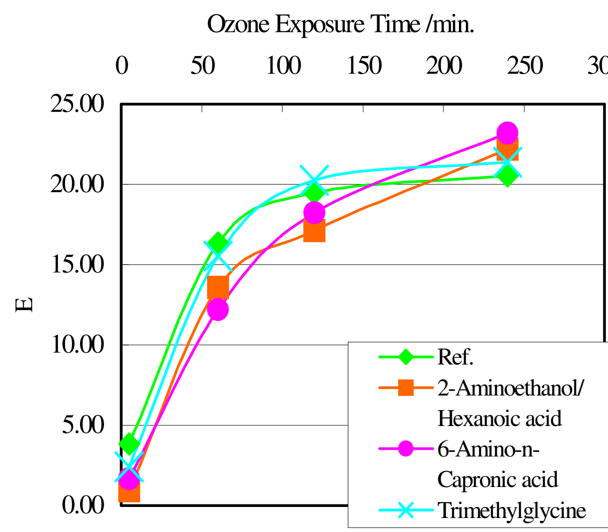

Figure 2. Ozone Fastness of Print with Amino Acids and Amine salt.

The quaternary amino acid had little effect on ozone fastness. This turned out just as we had expected from previous study by Chen-Ze Qi et al, because the quaternary amine has no lone pair electron on the nitrogen atom, it could not transfer the lone pair to ozone molecule for inactivation. To confirm the function of amines, different counter ions of carboxylic acid were examined (Figure 3).

Though alkali salt showed smaller color change than amine salt in a short time ozone exposure, the result was reversed after a long-term exposure. This result showed the importance of amines to improve the ozone fastness. The effectiveness of carboxylate salts in a short time ozone exposure was thought to relate to pH value of print surface. Ozone is known to oxidize many chemicals and produce acids. And phthalocyanine dyes are known to change color under acidic condition. So if the print surface had high pH initially, it would keep under alkaline condition even after a long time ozone exposure, and consequently it would keep its color unchanged.

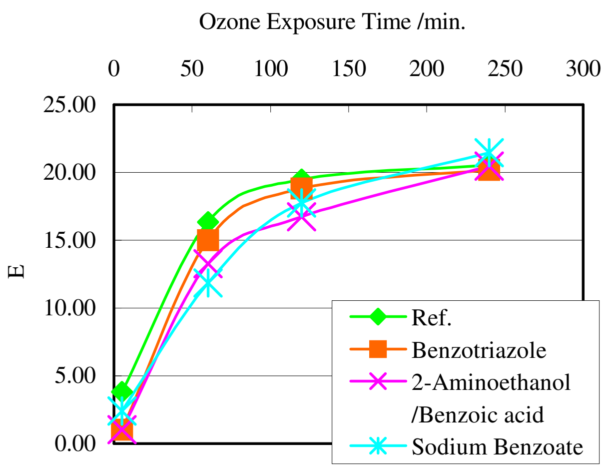

Figure 3. Ozone Fastness of Print Images with salts of a carboxylic acid.

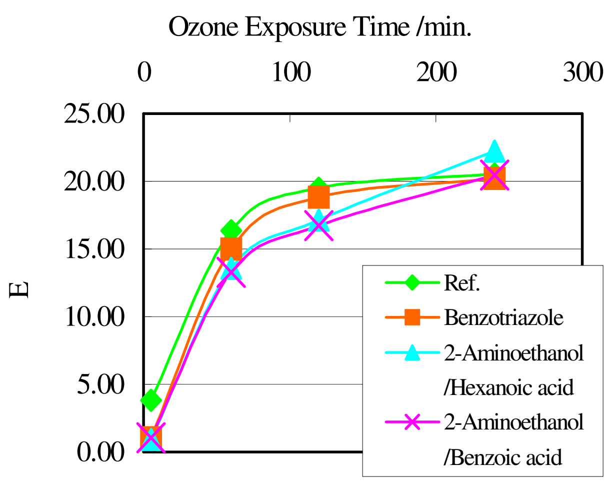

Figure 4. Ozone Fastness of Print Images with an Aliohatic Acid and an Aromatic one.

The effects of acid part of salts were examined (Figure 4). Aromatic acid was found more effective than aliphatic acid especially on a long-term ozone exposure as previously reported.[4]

Next, the effect of acid number of aliphatic acids and that of aromatic acid were both examined (Figure 5 (a) and (b)). As shown in figures, both monoacids were more effective than polyacids. The ozone fastness of print images could not be improved by increasing the number of carboxyl and amino group of the additive.

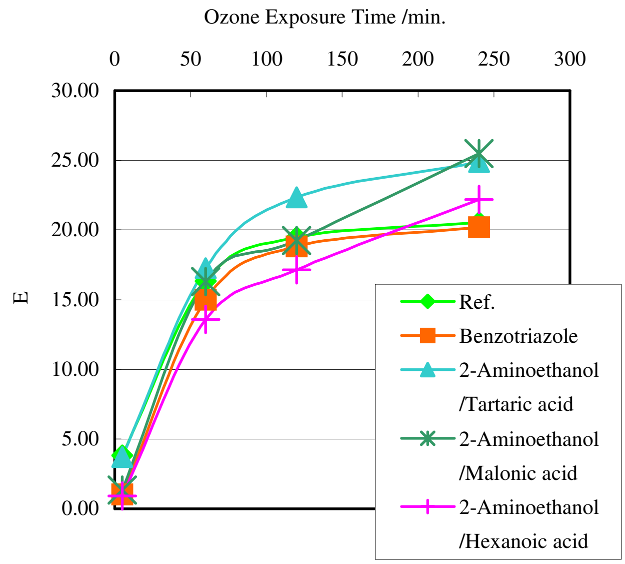

Figure 5(a). Ozone Fastness of Print Images with an Aliphatic Monoacid and Polyacid.

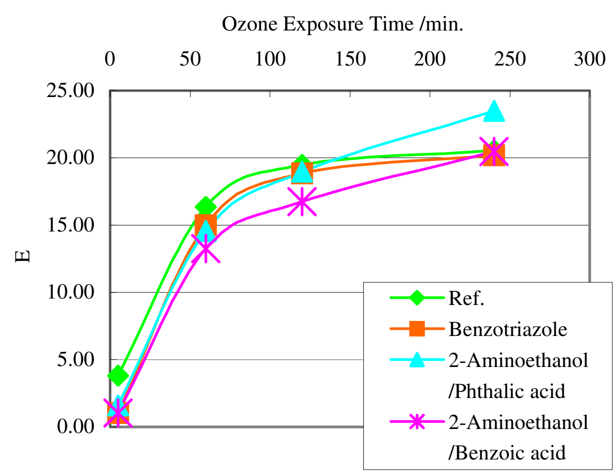

Figure 5(b). Ozone Fastness of Print Images with an Aromatic Monoacid and Polyacid

From these results about the effect of the different kinds of acids, parameters other than the number of carboxylic acid group might affect the ozone fastness of print images. As discussed above, the state of the lone pair electron on nitrogen atom would be important for ozone fastness. Therefore the acidity of the carboxylic acid, which differ the state of amine as a counter ion, was thought to affect the inactivation of amines. The relationship between the pKa values of the carboxylic acids and the hue change after ozone exposure (240min.) were examined (Figure 6). As expected, a negative correlation between them was observed.

This result confirmed us that the effect of ozone fastness depends of the state of the lone pair electron on the nitrogen atom of amine molecule, and that could be controlled by choosing suitable acid as the counter ion.

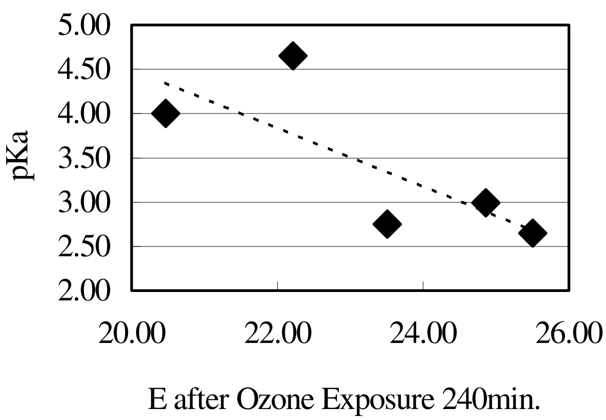

Figure 6. The Correlation between pKa of the Carboxylic Acid and Ozone Fastness of Print Images

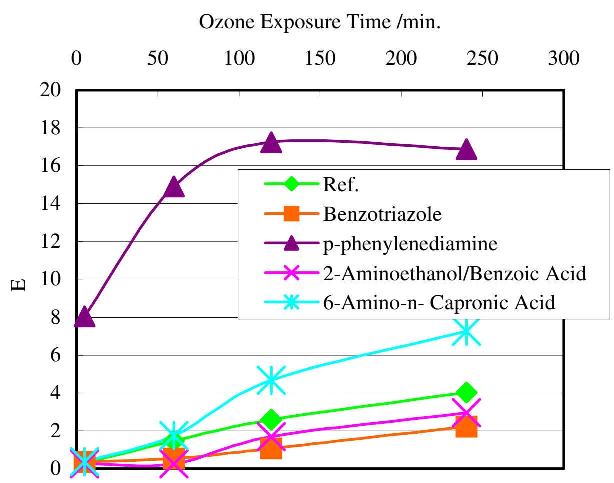

Figure 7. Ozone Fastness of Print Images with C.I. Direct yellow 132 and Additives.

In the next stage, we applied these results to azoic dye based inks. C.I. Direct yellow 132 was selected because it showed good hue and high lightfastness but suffers low ozone fastness. Benzotriazole, p-phenylenediamine, 6-amino-n-capronic acid, and 2-aminoethanol benzoate were examined as additives for this azoic dye based ink (Figure 7). 2-Aminoethanol benzoate and benzotriazole were almost equally effective on ozone fastness. From these results, we found that amine salts of carboxylic acid were effective on ozone fastness of variety kinds of dye.

Conclusion

We examined some kinds of additives to improve ozone fastness of prints on plain paper for phthalocyanine and azoic dyes. Antioxidants, amines, amino acids, and amine salts of carboxylic acid were examined. For phthalocyanine dye based ink, amino acids and amine salts of carboxylic acid were found to be effective to retard the color changing of prints by ozone. And the effectiveness of carboxylate salt was found to have correlation with the pKa of the carboxylic acid. This correlation confirmed us that the state of the lone pair electron on the nitrogen atom of amine molecule was very important for ozone inactivation. For azoic yellow dye, benzotriazole and carboxylic acid salts of amine were found effective to prevent color fading. Then carboxylic acid salts of amine were thought effective for improve the ozone fastness of dye based ink.

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Biography

Shigemi Wakabayashi received his B.S. in Applied Physics from Tokyo Institute of Technology in 1990, and his M.S. in Material Science form the same in 1992. In 1992, he joined Kao Corporation and had been engaged in research and development of magnetic recording media for two years. Since 1994, he has worked on ink jet colorants and inks.