Decolorable Ink

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Abstract

Decolorable ink developed by Toshiba consists of leuco dye, developer, and eraser. The key to fabricating an effective imaging material is to find a balance among these three components. There is equilibrium between colored leuco dye and colorless leuco dye. Because the equilibrium is dominated by colorless state in a solution, an addition of solvent to the ink instantly make it colorless. A similar decoloring process is performed by heating. This decolorable ink technology could be applied to almost all imaging materials.[1]

Introduction

Manufacturers of office printers have focused on the quality of printing. As a result, printing of excellent quality has been achieved and to the non-expert the quality of printing is indistinguishable among comparable printers. Thus printing technology has transcended the resolution of the human eye and the development of high quality printing is essentially over.

On the other hand, environmental considerations have emerged as a major issue. Many countries have enacted laws to protect the environment and the growing preoccupation with the environment is reflected in the changing purchasing patterns of consumers. In addition to the price of a product, consumer also has to consider the cost of disposal in 21st century. The more the disposal, the higher the cost tends to be. This trend is already evident and gaining momentum.

Predictions that the widespread use of personal computers and the rise of the Internet would reduce consumption of paper have proved to be false. In fact, as shown in Figure 1, the IT revolution has spurred demand for paper in Japan. This figure also indicates that demand for roll paper for newsprint has not decreased. In addition to this trend, as shown in Figure 2, the volume of final disposal sites in Japan has been decreasing from year to year. The strong objection of local inhabitants makes it very difficult to find locations where new disposal sites can be constructed.

A piece of paper could be trash because there is a disused image on the surface. If the ink is erased, the trash becomes a resource.

Therefore, the development of erasable ink is a basic proposition and is a possible solution to environmental problem relating to paper.

This keynote address introduces a decolorable imaging material, which can be applied to almost all kind of printing materials and writing instruments.

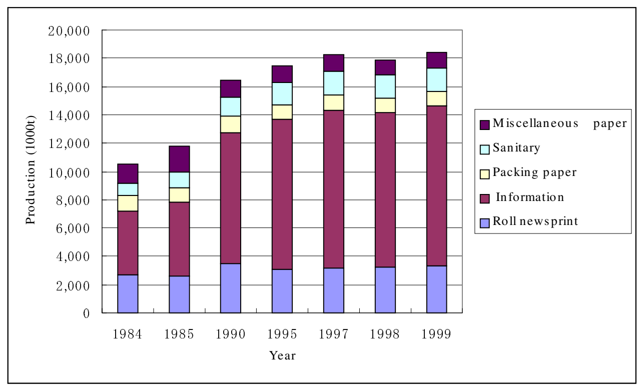


Figure 1. Production of paper in Japan
(Statistics of Ministry of Economy, Trade & Industry)

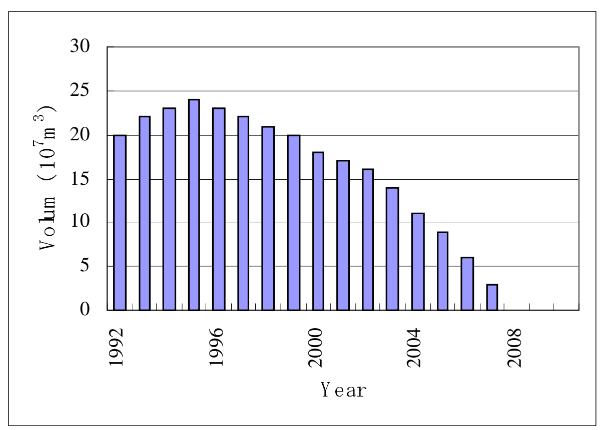


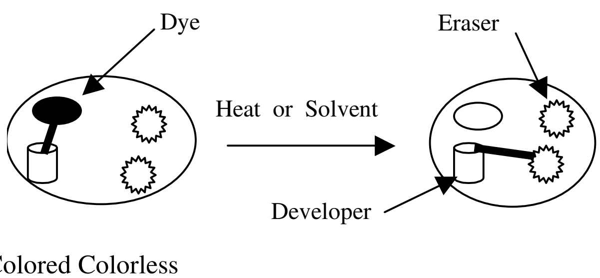
Figure 2. Volume of final disposal site in Japan
(Statistics of Ministry of Health, Labor & Welfare)

Principle of Decolorable Ink

The decolorable ink consists of three components such as dye, developer, and eraser. The leuco dye is originally colorless dye used in thermal paper.[2] The reaction between leuco dye and developer forms the color.

In the decolorable ink, colored leuco dye is used as well as the usual pigment of imaging material. The difference is the presence of eraser, which traps or absorbs developer in an erasing process.

There are two erasing methods, heat treatment and solvent treatment. In the case of solvent erasing, every component dissolves and the developer is absorbed in the eraser as shown in Figure 2.



(Unit of Imaging Material)

Figure 2. Principle of Decolorable Ink

The heat erasing can be explained in the same way.

Every component can move freely over the temperature of the melting point of the matrix, and the developer will be absorbed in the eraser.

Although solvent erasing is perfect erasing, use of solvent is limited to facilities equipped with systems for solvent collecting. In office, organic solvent is restricted to small-scale erasing, e.g. the use of an erasing pen to erase one character at a time.

The Equilibrium

The absorbance of colored leuco dye increased nonlinearly with increasing concentration. As shown by Figure 3, the absorbance did not follow Lambert-Beer's rule, unlike the conventional dyes. A typical black leuco dye, PSD-184[3] was examined, and a blue dye, Blue63[4] was examined. The developer used was n-propyl gallate (PG). It can be interpreted that there is an equilibrium expressed by equation (1). This behavior is not described even in the standard reference of leuco dye chemistry.[5]

Leuco dye : L, Developer: D

$$\underset{(Colorless)}{L + D} \overset{K}{\rightleftarrows} \underset{(Colored)}{L - D} \qquad (1)$$

The absorbance is apparently dominated by the colored species L-D, which has an equilibrium with constant K(=[L-D]/[L][D]). Therefore, observed molecular coefficient α included the equilibrium constant K in the following equation.

$$Abs = \varepsilon [L\text{-}D] = \varepsilon K[L][D] = \alpha [L][D] \qquad (2)$$

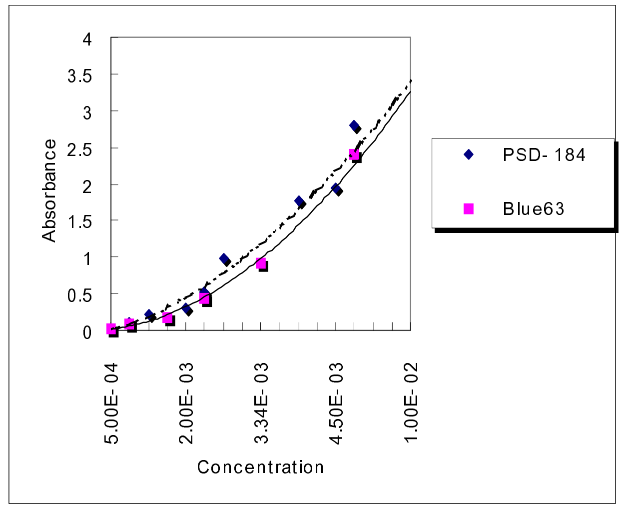


Figure 3. Absorbance change of leuco dye versus the concentration (mol/l).

We have estimated the molecular coefficient ε, based on the following hypotheses.

1) In acetic acid, acetic acid develops the color of leuco dye to 100%.
2) The molecular coefficient ε of fluorane dye does not deviate irrespective on the solvent.

The first hypothesis has been used to evaluate the absorbance of leuco dye. We have confirmed the second hypothesis with EtOH, CH_2Cl_2, acetone and acetic acid, by Rh6G, a dye of similar structure. Rh6G is not a leuco dye and it adheres to the Lambert-Beer's law concerning absorbance. The molecular coefficients were 11200 (at 530nm in EtOH), 10500 (at 520 in CH_2Cl_2), 9900 (at 525 in acetic acid), and 8700 (at 526 in acetone). No great deviation was observed in the case of using acetic acid as a solvent. Based on two hypotheses, the ε of PSD-184 was estimated to be 17600 mol/lcm. So the K of PSD-184 was estimated by equation (2) to be 5.1. Gibbs's free energy of this equilibrium was estimated to be -4.01 $\pm$ 0.38 kJ/mol. This is almost the free rotation energy value of a single bond. This value is smaller than value, -11.7kJ/mol, reported by Taguchi[6] for the decolored phenomenon of phenolephthalein-cyclodextrin complex. The structure of phenolphthalein is similar to that of fluoran leuco dye, and it is well known that its color changes depending on PH and environmental factors. We have examined Blue63 in the same manner. The ΔG was -4.10 ±0.38 kJ/mol. The result means that the ratio of colored dye was 5% at 1×10^{-2} mol/l. It means that 95% of leuco dyes did not contribute to the color formation at relatively higher concentration. As a result、the decrease in absorbance was inversely proportional to the [L][D] when the solution was diluted. We have reported[7] the precise analysis of the equilibrium by NMR.

$$L - D \overset{Solvent}{\rightleftarrows} L + D \quad (3)$$

$$D + E \rightarrow D - E \quad (4)$$

$$\text{or} \quad L + E \rightarrow L - E \quad (5)$$

Therefore、the color of imaging materials on the paper is decolored rapidly by added solvent. The decoloring process is interpreted as follows. The added solvent on the paper dissolves the colored leuco dye and developer and the contents of the coloring material are diluted and dye and developer separate from each other as described by equation (3). The next step is absorption of components by the eraser as described by equation (4) or (5).

Fixing Process

For the complete decoloring, fixing of the colorless state is very important. The key material is the eraser defined as an absorber of other components. The requirement for the eraser is that it has an ability to make a chemical or physical interaction with leuco dye or developer. In an ideal system, the interaction would be stronger than the chemical bond between leuco dye and developer. The interaction would be sufficiently weak not to erase the ink before erasing. Or the interaction must be frozen in the making process. We have chosen a method of crystal packing of cholesterol, for example. In a kneading process of leuco dye, developer, and cholesterol, the cholesterol is dispersed as a small crystal after the kneading. The heat erasing process causes the crystal to melt and activate as an eraser. The solvent dissolves the crystals and activates them. Separation by microcapsule is another candidate method to confine the activity of eraser.

Toner for Electro-Photography

We have developed toner for copiers or printers. In this development, the main task is to improve the quality of printing. We have focused on the improvement of the image density and the erased quality. As mentioned above, the decolorable toner (ink) contains eraser, which could reduce the image density at the fabricating process. Therefore there is much know-how to produce the decolorable toner. We have achieved the density of more than 1.0, and the running test up to 30000 copies for both black and blue toner.

Concerning the erasing method, we have examined the erasing of a bundle of 200 sheets at once by oven-type dryer. The temperature is 130℃ for 2 hours. As mentioned above, colorless toner remains on the surface of paper, which can be read by changing the view angle. The visible density is the same as transparent image of backside printing. For the heat erasing, we propose the use of exhausted heat from a facility such as a co-generating system, a power plant, or a boiler.

Other Imaging Materials

Because Toshiba is not a manufacturer of ink or stationery, we have transferred our technology to several ink and stationery companies. Those companies are developing commercial products. There are companies that have advanced trial products such as ballpoint pens, ink-ribbons for thermal printers, ink-jet ink and other conventional ink.

We estimate the degree of difficulty in development to be in the following order;

Most difficult: Offset ink > Gravure ink > Ink-jet ink > Marking pen ink > Ballpoint pen ink > Toner > Ink-ribbon ink > Solid ink (ex. crayon).

The above order relates the minuteness of ink particles. In the case of offset ink, the printing quality requirement is 2400 dpi, i.e. for ink particles of sub micron. The requirement for ballpoint pen ink is similar.

Our goal is popularization of decolorable ink. For this purpose, diffusion in small products is the first step. The second step is application to the use of computer related printing in our office. The last step is application to newspaper and magazine printing.

Reuse or Recycle

There is a person who would not believe the effectiveness of decolorable ink, and likely impact on society. There is a trauma in manufacturer of printer to kind of erasable toner, because the former commercialized product was not used at all. We have to analyze reason why the former method was not used.

We think the reasons are as follows;

1) Limitation of color
2) Limitation of stationery goods
3) Limitation of printing method
4) Imperfect erasing
5) Cost
6) Sheet by sheet erasing
7) Troublesome feeling
8) Times: It was too early

We think reasons 1) to 6) do not apply to our decolorable ink.

Concerning the reason 7), even in the case when we do nothing for the disposed documents printed by the decolorable ink, it would contribute to the saving resources, because it would be automatically de-colored in early stage in the usual paper reclaiming process, such as a process in which the paper is passed through a hot alkaline solution. The plant has many sensors to measure the amount of colored materials and would regulate power, chemicals and water in the de- inking process. Decolorable ink could be used in exactly the same way as conventional imaging material, but it would contribute to the environmental preservation. People motivated by environmental concerns could reuse each sheet of paper several times. Even if paper were reused only once, the saving of resources would be considerable and quantity of paper trash would be reduced significantly.

Conclusion

The basic proposition *to develop erasable ink* is realized by the decolorable ink comprising dye, developer and eraser. There might be other methods of recycling paper much more effectively, but we think ours is the method likely to win widespread acceptance in society.

At present, decolorble ink is costly compared with carbon black ink. However decolorable ink can contribute the preservation of forests and reduction in CO_2 emissions, since it enables paper to be used several times and the de-inking process to be compressed, thereby saving energy. As a result, decolorable ink can tribute to a reduction in the amount of waste incinerated. Therefore, the cost disadvantage of decolorable ink may become a negligible factor in the near future.

References

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2. For example、thermal paper (thermo-sensitive recording paper) is used for cash register receipts. Thermal paper consists of leuco dye and excess amount of developer (color forming component) which makes image development easy.
3. PSD-184 (Nippon Soda Co., Ltd.): 2-anilino-6-(N-ethyl-N-isobutylamino)-3-methylfluoran; CAS No.95235-29-3
4. Blue63 (Yamamoto Chemicals Inc.):3-(4-diethylamino-2-ethoxyphenyl)-3-(1-ethyl-2-methylindol-3-yl)-4-azaphthalide; CAS No. 69898-40-4.
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Biography

Kenji Sano is a chief research scientist at Corporate Research and Development Center, Toshiba Corp., Kawasaki, Japan. He received the BSc degree from Tokyo University of Agriculture and Technology in 1979 and Doctorate from Tokyo Institute of Technology in 1985 for work on organometallic compounds. He joined Toshiba in 1985 where he has been engaged in the development of organic photoconductors for electro photography, organic electro luminescence devices, and basic research on control of molecular orientation, and liquid crystal devices. He is currently with the Display Materials and Devices Laboratory at the Corporate Research and Development Center. His current research interests are the decolorable ink and unicolor woven barcode. For his work on decolorable ink, in 1999 Dr. Sano received the Asian Innovation Award, and the Encouragement Award from Science and Technology Agency. In Japan, the decolorable ink is briefly introduced in a science textbook for use in junior high school.