Rewritable Printing System Using Leuco Dyes

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Abstract

Printing systems that are capable of displaying information are becoming increasing important as greater volumes of information become available in digital format. But considering that most documents are only printed for temporary use then discarded, a rewritable printing system would be useful and advantageous for the environment. We have now succeeded in developing a practical rewritable printing system that is capable of rewriting the same sheets more than 500 times. By thermally controlling the coloring reaction of leuco dyes, the system creates stable, high-contrast color images that can be quickly erased so the sheets can be reused and overwritten with new images. This is made possible by our ability to control molecular aggregation structures formed by long-chain molecules in leuco dye developer, which opened the way to our development of functional reversible media based on the supramolecular structure of leuco dye and the long-chain developer.

Introduction

Paralleling the widespread digitization of information in recent years, we are seeing a major transformation where the traditional role of paper as the main medium for recording and conveying information is being taken over by the role of displaying. Still a far greater amount of paper continues to be used than ever imagined, most of which is used to display information temporarily then discarded. It was in this context that the concept of *electronic paper* was first proposed, and a variety of different systems—electrophoresis, liquid crystal, and others—are being actively investigated with the goal of developing a kind of electronic paper. But the reasons we use so much paper are that paper is easy to handle and can be perused at a glance, attributes that are lacking in electronic paper based on the same technologies as digital displays.

Considering that the vast bulk of printed hardcopies are just used for a short time and then discarded, society is quickly coming to see the need for systems that permit images to be printed then erased and the medium reused over and over again. A print system that can be rewritten and reused many times and that resembles the paper hardcopies we are all used to could provide the functionality of a *new paper* that is suitable for the digital information age.

Seeking a medium that can be rewritten many times, our work has focused on leuco dyes capable of shifting from a colorless state to an intense color, and now we have developed a practical rewritable print system based on these dyes that can be applied to a wide range of applications. Although the coloring/decoloring reaction of leuco dye has been known for a long time, it was only recently that we came to understand how this reaction could be controlled by molecular aggregation, and exploit this property in the development of a new rewritable printing application.

Coloring/Decoloring Control of Leuco Dye

At the very minimum, a practical rewritable printing system must be capable of (1) forming clear, high-contrast images, (2) maintain stable displayed images, and (3) fast and easy erasing and rewriting. The ability to form sharp black images against a white background is particularly important for good image quality. To achieve such a system, we focused our efforts on ways to control the reversible coloring/decoloring reaction of leuco dye with heat. Leuco dyes change from a colorless state to a colored state through a reaction with an acidic compound (called the *developer*), and this reaction is used by thermal recording paper. The reaction is reversible as one can see from Fig. 1, but the material system used in conventional thermal paper cannot be erased at one's discretion after an image is formed.

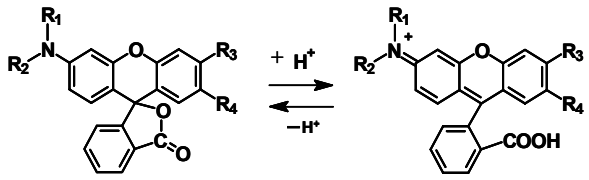

Figure 1. Leuco dye reversible color reaction

The reversible coloring materials for rewritable printing must provide good stability in both colored and colorless states, and must allow rapidly decoloring whenever the user requires. Formerly, a chemical reaction between dye and developer was always used to bring out the colored state of leuco dye, but we were primarily concerned with the relationship between the dye and molecular aggregation state of the developer. Realizing that the color disappears if the developer is separated from the leuco dye, we tried to further the separation from the dye by

introducing long-chain structures that allow the orientation and increase intermolecular aggregation force of the developer. The intermolecular aggregation force promotes crystallization of the developer which hastens separation from the leuco dye. Based on this work, we were able to construct the first practical reversible color molecular system that works under thermal control. [1]

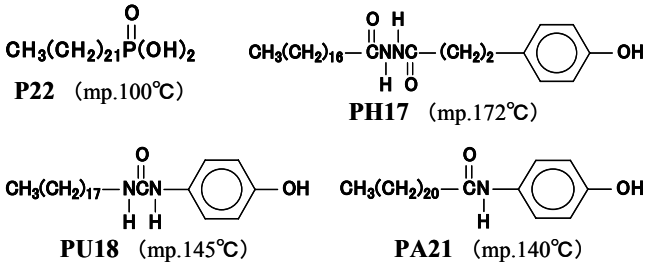

Figure 2. Long-chain developers providing reversibility

The first developer we found that is capable of controlling the coloring/decoloring process was docosylphosphonic acid shown in Fig. 2. Subsequently it was found that the phenolic compound in Fig. 2 having long-chain alkyl groups and associative groups formed intermolecular hydrogen bonds yielded the same reversible coloring performance. Figure 3 shows the coloring and decoloring processes of the composite comprised the long-chain developer and leuco dye. If heat is applied to the composite in a decolored state (A), it enters a melted state (B); then if the melted state composite is quenched, it shifts to a solid colored state (C). Then, if the colored composite (C) is reheated to a temperature less than the melting temperature, the color disappears (D-E), and if allowed to cool in this state, returns to the decolored state (A). If the composite in the melted state (B) is allowed to cool down slowly, the color disappears as the material cools. The temperature range at which the color disappears differs depending on the molecular structure of the developer.

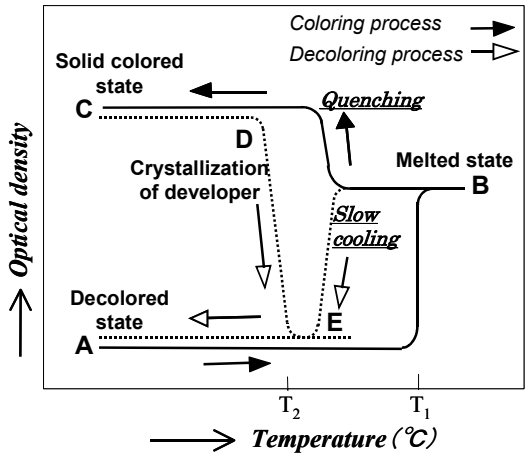

Figure 3. Coloring/decoloring processes of leuco dye/long-chain developer systems

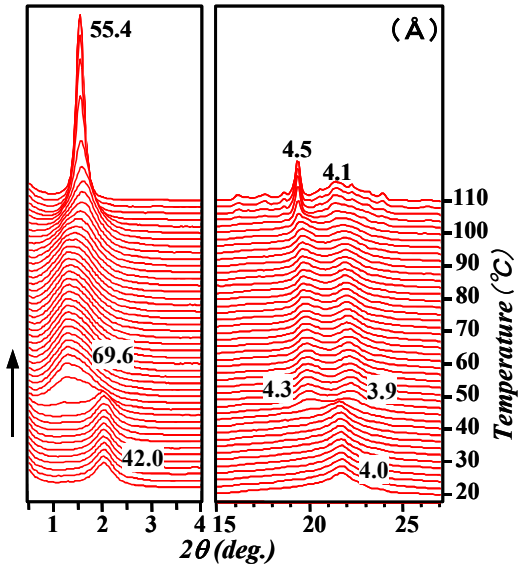

Figure 4. X-ray diffraction spectrum changes during decoloring of leuco dye/long-chain developer PU18 composites (syncrotron radiation X-ray diffraction, temperature increase at rate of 2℃/min)

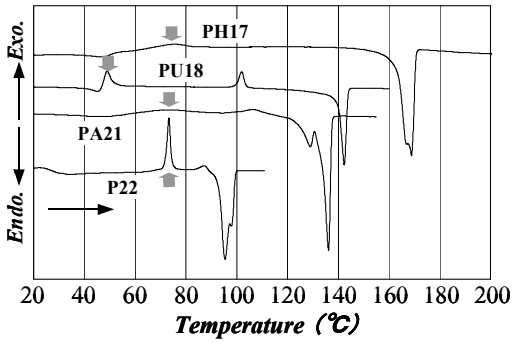

Figure 5. DSC heating thermograms of leuco dye/long-chain developer coloring composites at a rate of 5℃/min (arrows are exothermic peaks according to decoloring)

The developer used in ordinary thermal paper that is not reversible does not contain the long-chain structures. Moreover, the colored state of these composites containing leuco dye are tar-like and do not readily become a solid. By contrast, the colored state of composites using the long-chain developers described earlier does become solid, which is presumably related to the molecular aggregation state. X-ray diffraction analysis revealed that in the colored state these composites form a layered lamellar structure with the long-chain molecules aligned in the same direction, while the decolored state coincides with the independent crystalline structure of the long-chain developer. X-ray diffraction while increasing the temperatures revealed that at the temperature where the composite shifts from colored to decolored state, the lamellar structures abruptly give way to developer crystallization, and a exothermic peak is

observed by differential scanning calorimetry (DSC) corresponding to this temperature where the color disappears. For example, Fig. 4 shows the structural change of the colored composite using the long-chain developer PU18 as the temperature is increased observed by X-ray diffraction. Figure 5 shows DSC readings as the colored composite is heated using the long-chain developers shown in Fig. 2. Note that a defined exothermic peak can be observed at the transition temperature where the composite is decolored regardless of which long-chain developer is used. In the case of developers PA21 and PH17 characterized by gradually disappearing color as temperature is increased, the exothermic peaks are flattened.

It will be apparent from these results that the coloring/decoloring of materials consisting of leuco dye and long-chain developer can be attributed to the mechanism illustrated in Fig. 6. When the composite in the melted state (B) is quenched, the leuco dye is incorporated into the lamellar structures formed by the long-chain developer, and both are bound together in a solid colored state (C). When the temperature of this colored material is increased, the lamellar structure starts to collapse, the long-chain developer assumes its most stable crystalline form, and the expelled leuco dye becomes colorless. In these coloring and decoloring processes, the intermolecular aggregation force of the long-chain developer contributes to both the stability of the colored state and the rapid transition to the colorless state.[2, 3]

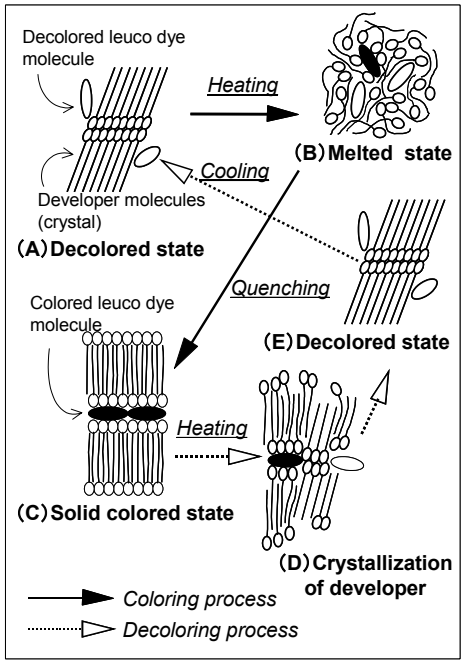

Figure 6. Coloring/decoloring mechanism of leuco dye/long-chain developer systems

From a close examination of the x-ray diffraction spectra, it is apparent that the spacing between lamellar layers in the colored state is narrower than the spacing between lamellar layers of the developer crystals. The spacing of the developer crystal lamella layers in the decolored state is determined from the length of two developer molecules associated with the phenolic group, while in the colored state the spacing is equal to the length of one molecule of the long-chain developer plus the thickness of the leuco dye. Presumably this is why the long-chain structures of the developer are lined up like the teeth of a comb as shown for the colored state in Fig. 6(C). This kind of structure is inherently unstable as a long-chain molecule, which suggested that temperature raising causes the comb-like structure to dissolve and revert to the more stable crystallization of the developer, which triggers the transition to a decolored state.

Development of Practical Materials

All of the long-chain developers introduced in Fig. 2 can control reversibility between colored and decolored states, but are lacking in one or another of the properties required for a practical medium "Rewritable Paper". The phenolic developers in Fig.2 can rapidly erase, but the color state stability of PA21 and PU18 are insufficient, and it is difficult to obtain sufficient color density from developer PH21.

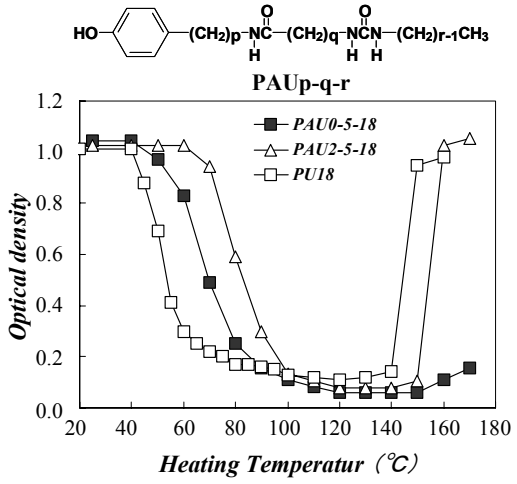

Figure 7. Typical structure of long-chain developer with enhanced intermolecular aggregation force and erasing temperature characteristics of rewritable medium using the developer

To obtain a developer with all the ideal attributes—high color density, good stability of the colored state, and rapid transition to the decolored state—we designed new long-chain developer molecules. We observed earlier that the driving force of both coloring and decoloring processes of composites made of leuco dye and long-chain developer is the intermolecular aggregation force in the developer. Our objective therefore was to increase the intermolecular aggregation force of the developer. Essentially what we tried to do is incorporate more associative groups that

function to form hydrogen bonds between the long-chains units of the developer molecule. Figure 7 shows one basic structure of the designed long chain developer and the thermal characteristics of erasing. The figure plots the optical density depending on applied heating temperature after a colored medium was heated by a heat block for 1 second. One can see that compared to developer PU18 that has only one associative group (urea group) in the long chain unit, the starting point of decoloring shifts toward higher temperature and thermal stability increases in the colored state of developers PAU0-5-18 and PAU2-5-18 with two associative groups—a urea group and a amide group—connected by a polymethylene group of suitable length. In other words, rewritable medium using the developer with two of these associative groups shows little loss of image density even when saved in a 50ºC environment. Transition to a colorless state is also very fast; with application of heat at the right temperature, images are erased in less than 0.1 second.[4]

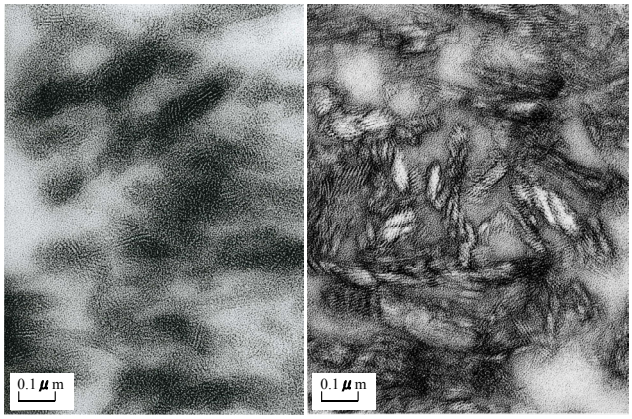

Figure 8. Cross-sectional TEM observations of reversible coloring layer using leuco dye/long-chain developer PAU0-5-18 system

Using a heat roller or other heater-based erasing mechanism, a rewritable medium that could be fully erased within several tens of milliseconds applied heat would be more than adequate for practical applications. However, we would have to accelerate the erasing process by at least an order of magnitude if just a thermal head is used for the heat source, since any rewriting mechanism that erases the previous image and prints a new image at the same time requires several milliseconds of heating time. When energy of 2-millisecond pulse width is applied by an erasing unit using a thermal head, the image density of the rewritable paper using developer PU18 with one associative group was reduced to about 40% while the image density using developer PAU-0-5-18 with 2 associative groups was reduced to about 20%. The fast erasing property of the rewritable medium using developer PAU0-5-18 is presumably related to the molecular aggregation structure of the colored state. X-ray diffraction analysis revealed that the peak based on spacing between lamellar structure layers that we saw earlier for PU18 and other developers could hardly be discerned for the colored composite consisting of leuco dye and PAU0-5-18. However, a layered structure in the colored state is detected by the transmission electron microscopy (TEM) images in Fig. 8, so here too a lamellar structure is formed even though it is too small to be detected by X-ray diffraction. From these results we can infer that the lamellar structure domain of the colored state formed by the PAU0-5-18 is small, so developer crystallization during the erasure process occurs in high density by small units, so erasing proceeds quickly overall.

Rewritable Paper Performance and Print System

Figure 9 shows the structure of rewritable paper using the basic long chain developer structure shown earlier in Fig. 6. Ordinary fluoran compound was used for a black-coloring leuco dye, and white PET film was used for the substrate. A protective layer of hardening resin with embedded inorganic particles was applied on top of the thermo-reversible coloring layer to ensure the material could withstand the thermal and mechanical stress owing to rewriting several hundred times. A matrix of hardening resin was also applied on the reversible coloring layer and the coloring material was distributed in the cells of the matrix. This rewritable paper has already found a number of practical applications in Japan including the information display portions of magnetic cards and IC cards.

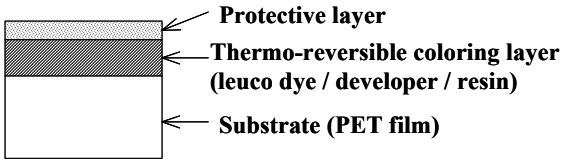

Figure 9. Basic structure of rewritable paper

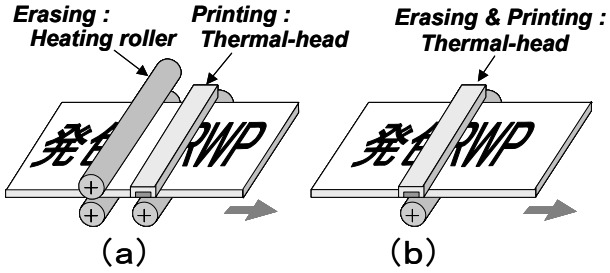

Figure 10. Print systems using rewritable paper

Figure 10 shows schematics of two printing system that use rewritable paper. Figure 10(a) shows a configuration in which an ordinary heater roller is used to erase the previous image at approximately 140ºC followed by thermal-head that imprints the new image. Figure 11 shows a photograph of a printer implementing the scheme illustrated in Fig. 10(a). Using this printer, the paper can be rewritten more than 500 times. Figure 12 reveals that the

image density and the density after erasing remains practically unchanged even after the paper is rewritten up to 500 times. The color image is also extremely stable, so the color density remains undiminished for at least several years under normal environmental conditions.

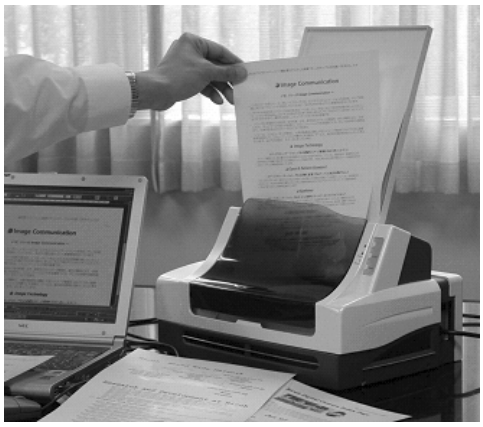

Figure 11. Rewritable paper print system in use

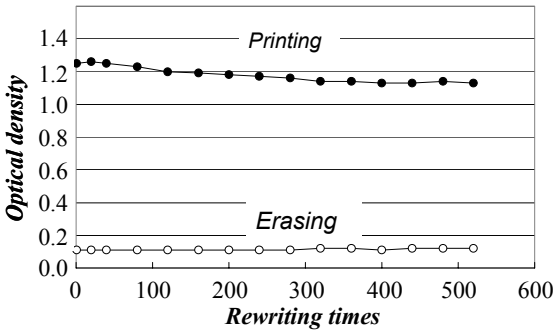

Figure 12. Variation in image density and density after erasing as a function of number of rewriting times

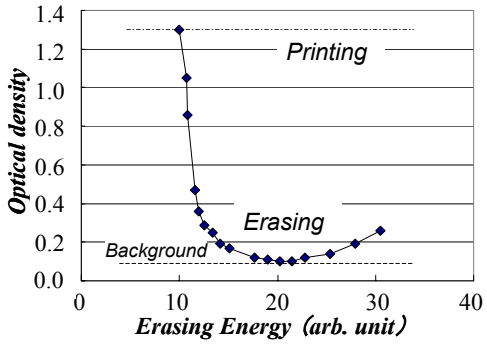

Figure 13. Erasing characteristics of rewritable paper based on overwrite scheme

Figure 10(b) shows a configuration in which overwriting is done by a thermal-head. Some of the thermal-head's heating elements apply energy to imprint a new image, while other heating elements apply energy sufficient to completely erase the image. This permits the previous image to be erased and a new image formed with just a single pass through the thermal head. Figure 13 shows the erasing performance of our improved rewritable paper for thermal head overwriting. By applying the right amount of energy, erasing of the previous image is virtually complete. Adopting this kind of overwrite mechanism, a more compact printer can be implemented that consumes less power.

Conclusion

Although the coloring and decoloring of leuco dyes involves a chemical reaction, we found that the chemical reactions of leuco dyes in combination with long-chain developers could be controlled by physically changing molecular aggregations. There was little awareness until now that the very different colored and decolored states could be selectively formed by changing aggregation states made of two kinds of molecules. Realizing a breakthrough in reversibly, one of our key objectives in developing image-forming materials based on this molecular system, we have developed practical rewritable paper that can be erased and reused over and over again.

When people want to use digital information in their thinking and decision-making, it is very commonplace today for people to unconsciously print out. We believe that rewritable paper could be very effective for printing out these kinds of documents that are only used temporarily then discarded. While some may disagree as to whether rewritable paper is applicable to the concept of electronic paper, using this rewritable printing system as a means of paper-like display could become a form of electronic paper, say through fusion with a digital technology like IC tags.

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Biography

Kyoji Tsutsui received his doctorate in physical chemistry from Hiroshima University in 1995. He joined Ricoh Co., Japan in 1975 and has done considerable work on materials for electrophotography. Since 1985 he has worked in the field of materials for reversible recording. Mr. Tsutsui is Senior R&D Engineer at Ricoh Co. and a member of the Chemical Society of Japan.