Dual Color Leuco Type Thermal Rewritable Marking

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Abstract

Leuco type thermal rewritable media (LTRM) is based on traditional technology of direct thermal printing. However the introduction of an erasing process brings a rich diversity into its properties and as such requires new understanding of the dynamics of the microscopic structural transitions in order to design practical recording material. The key issue in LTRM is to control its cooling rate during amorphous-to-crystalline transformation. In this report we will discuss the mechanism of the amorphous-to-crystalline transformation in LTRM and will demonstrate the concept of dual color thermal recording by using two different rewritable recording layers with different cooling rate dependency.

Introduction

Rewritable Paper is somewhat different from Digital Paper because it needs an external device, such as a printer, to apply and renew visible information on it. Therefore Rewritable Paper can not be used like a display and is not the likely winner of Digital Paper but it is still interesting and useful technology for human life. There are two major benefits of rewritable paper. First, it can provide an environmental friendly system by reducing an amount of paper waste. Although recycling paper is beneficial from the viewpoint of material consumption, it is not so advantageous from the viewpoint of energy consumption. There is also economical reason in reusing paper by utilizing the rewritable paper since one can reduce the total printing cost. The other benefit is that it can provide an easier way for updating visible information. The rewritable card applications are excellent examples of this benefit.

There are many types of technologies that could be Rewritable Paper available. But thermal rewritable media may be the most successful technology in practical usage so far. Thermal rewritable media are classified into mainly two different types. One is transparent-opaque type[1] and the other is Leuco dye type. The transparent-opaque type was a pioneering material and has been widely used for mainly loyalty card application. On the other hand, Leuco type rewritable media is a relatively new material. Since Leuco type is based on traditional direct thermal media, it resembles traditional paper media more than the Transparent-opaque type. Leuco type can realize high contrast and high resolution with white background. Thanks to these advantages, Leuco type has been expanding its applications from card application to RFID (Radio Frequency Identification), Rewritable Paper application in Factory Automation field and information boards.

The key issue of Leuco type rewritable media is to control the cooling speed following application of heat to switch from a colored state to a decolored state and vice versa. If we positively utilize this cooling rate dependency, it is possible for us to realize the condition that one rewritable recording layer is in printing mode and the other rewritable recording layer is in erasing mode at same time.

In this report we will discuss molecular design of rewritable developers and demonstrate the dual color LTRM.

Printing and Erasing Process in LTRM

Figure 1 illustrates how the image density of LTRM changes with temperature of the system , which consist of Leuco dye and developer. Once the system is heated up to the melting points of these compounds, the melted mixture of these compounds will be obtained. The final state of this melted mixture depends on the cooling speed of the system. When the cooling speed is high enough, the final state will be an amorphous colored state. On the other hand, when the cooling speed is low, the crystallization of the developer becomes the dominant process, and the system results in a crystalline decolored state. The decolored state can be also realized by an application of heat, followed by slow cooling, to the amorphous colored state at the temperature of below melting point (dotted line). This process is explained as amorphous-to-crystalline transformation.[2]

Molecular Design of Developer and Print-Erase Property of LTRM

The print-erase property of LTRM highly depends on the molecular structure of the developer, which is typically phenolic compounds with a long alkyl chain. Figure 2 shows representative developers that we have developed.

Although Dev.1 is a very simple compound, it exhibits an excellent print-erase property. However, in practice, it requires a long erasing process time (slow erasing rate). Dev.1 also has a disadvantage in the heat stability of the image for practical usage.

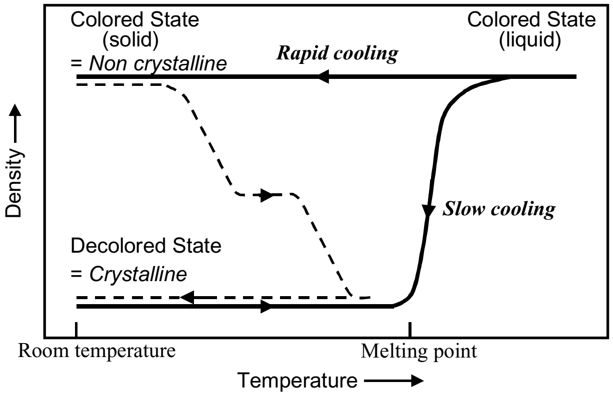

Figure 1. Coloring/Decoloring process of ThermoRewrite.

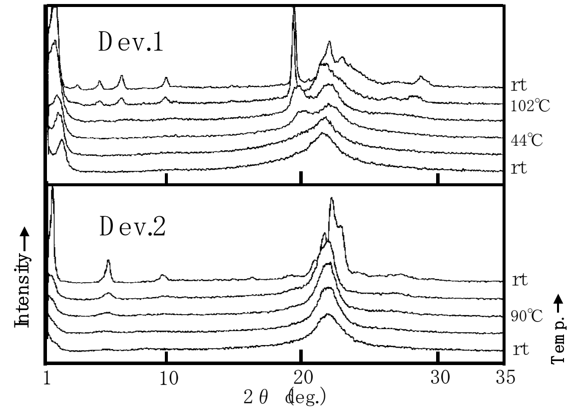

Figure 3. Change in X-ray diffraction pattern of the Dev.1 and Dev.2 increasing temperature of the colored state mixture.

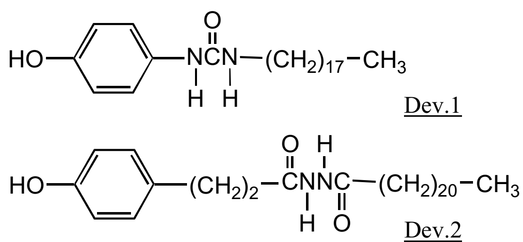

Figure 2. Structural formula of developers.

Improvements in the heat stability of the image can be expected by improving the cohesion force between developers. On the other hand, regarding erasing rate, the rate of the developer's crystallization has to be improved. Dev.2 was designed base on these points of view. To improve the cohesion force, the Docosyl group was replaced with an Octadecyl group. As for the erasing rate, the urea group was replaced with a diacyl-hydrazine bond. Since N,N'- diacyl-hydrazine group makes intermolecular five-membered hydrogen bond formation, it results in a small steric hindrance and a strong intermolecular hydrogen bond. In addition to these modifications, the ethylene group was introduced between phenol group and diacyl-hydrazine group so that the molecule has enough flexibility between functional groups. As a result, Dev.2 has excellent heat stability and erasing rate.[3]

Analysis of Amorphous-to-Crystalline Transformation

The microscopic structural change in LTRM was analyzed by X-ray diffraction and DSC measurement. The colored state mixture of Leuco and Dev.1, or Dev.2 were prepared as a staring material. Figure 3 shows the change in x-ray diffraction pattern as the each colored state mixture is heated up to around 100 Celsius then cooled slowly down to room temperature. Figure 4 is DSC curve of colored mixture.

In the case of the colored state mixture with Dev.1, changes in diffraction pattern were observed at 44 Celsius and 102 Celsius at which temperature DSC also shows the exothermic peak, suggesting two structural transitions during the heating process. At the temperature of 102 Celsius, the mixture is already in a decolored state and has crystalline structure according to the x-ray diffraction pattern.

At the beginning, the colored state of both mixtures show broad peak at $2\theta=22°$ in its x-ray diffraction pattern, which corresponds to spacing of about 4Å. Since this spacing is comparable to the spacing for parallel alignment of the long alkyl group, it is suggested that the colored state mixture at the temperature below 40 Celsius, is not in pure amorphous state but still possesses low level structural order. (in this report we call this Low Order Aggregate LOA)

In the region between 49 Celsius to 102 Celsius, although the optical density of the mixture drops in some degree, it never reaches the complete decolored state. Based on this observation, we assume that the mixture is in some intermediate situation between Crystalline state and LOA in this region of temperature. (HOA, High order Aggregate)

We attribute the poor heat stability of Dev.1 to that the ease of the phase transition from LOA to HOA in this system. The low erasing speed of Dev.1 can be attributed to requirement of a relatively large energy for the transition to the Crystalline state.

As compared to Dev.1, Dev.2 shows different characteristics in both of X-ray diffraction and DSC curve. In the case of Dev.2, from visible observation, the transition from the colored state to the decolored state can be recognized at 90 Celsius. However, no change in x-ray diffraction spectra and DSC curve can be observed. DSC curve for the mixture with Dev.2 shows a single peak at Dev.2's melting point. This means in the mixture with Dev.2, the transition from the colored state to the decolored state is associated with no microscopic structural change. We assume, the main reason for the higher erasing rate in Dev.2 is that both of the colored state and the decolored state can be formed in same LOA state.

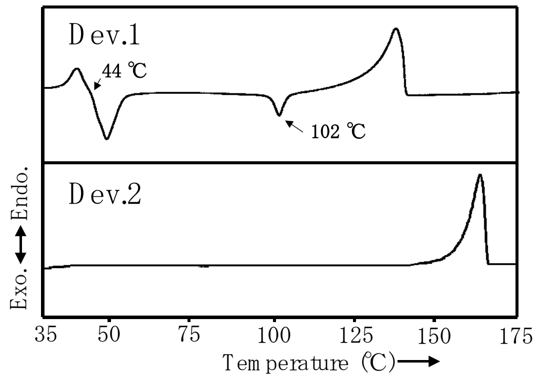

Figure 4. DSC curves of the Dev.1 and Dev.2 in the colored state mixture.

Measurement of Erasing Speed

From above discussion, now we know there are two different routes in the erasing process. One is the path in which the erasing process is associated with microscopic structural change at the same rate, which corresponds to the case of Dev.1. The second is the path in which the erasing rate is much faster than the structural phase transition, like in Dev.2. How much qualitative difference in the erasing speed can be expected between two developers?

To answer to this question, we estimated the erasing rate by monitoring how fast we need cool down the melting mixture to obtain the colored state. The procedure of this experiment was as follows. The mixture of dye and developer were heated up to the melting point first in order to create the melted mixture. As the temperature of system and optical density were monitored, water at specific temperature was doused on the mixture to cool it down. Then resultant cooling rate and final optical density of the system was determined for different temperatures of water. Figure 5 is the obtained cooling rate dependency of the formation of the colored state for each Dev.1 and Dev.2.

As a result, Dev.1 require at least 50 C°/sec to form the colored state. On the other hand, Dev.2 need more than 200 C°/sec. Since the formation of colored stated is the opposite direction to the erasing process, we assume these values are also an indication of an estimation of the erasing rate.

Concept of Dual Color LTRM

What if the two layered LTRM, one layer with Dev.1 and the other layer with Dev.2, experience the cooling rate of 100 C°/sec? This is the key idea for dual color LTRM. Since the system with Dev.2 can not form colored state at this cooling rate, only the layer with Dev.1 can be colored. This is the remarkable difference from a traditional dual color thermal media In the traditional system, it is not easy to print both color independently because the printing energy for the color with lower sensitivity, it is usually black, can also result in image of the color with higher sensitivity, blue or red color, simultaneously. As a result, a black image is not real black but the mixture of black and red, or black and blue.

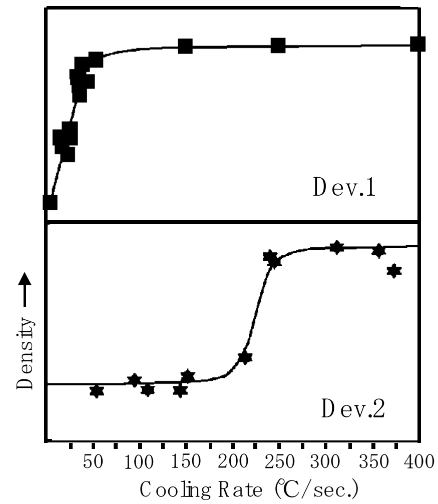

Figure 5. Cooling rate dependence of the formation of the colored state.

Figure 6 shows the layer structure of dual color LTRM. The top layer is rewritable recording layer which consists of the developer for high cooling rate such as Dev.2 and the bottom layer contains the developer for low cooling rate such as Dev.1. The intermediate layer (control layer) works as a separator between two layers and is used also to tune the difference in printing sensitivities between these layers. As shown in Fig. 6, in this report, top layer is blue image layer and bottom layer is red image layer.

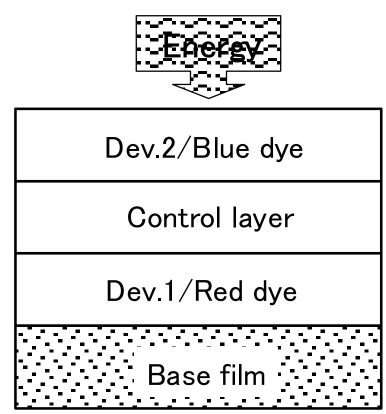

Figure 6. Layer structure of Dual color LTRM.

The procedure of dual color printing is as follow

(1) Erasing whole area of both layers at same time.
(2) While the blue image layer is still relatively hot, printing red image with enough power to get image on bottom layer. Under this condition, the resultant cooling speed in blue image layer is less than 200°C/sec because

of initial temperature of the system, then no blue image is obtained.

(3) Finally, after the temperature of the top layer reaches near room temperature, the top layer is printed with less energy which can generate the image only in the top layer.

Conclusions

In this study, we discussed the print-erase mechanism in LTRM showing how cooling rate of the system is important to control its final state. We demonstrated the molecular design of the rewritable developer based on this theory and analyzed microscopic structural change by using x-ray diffraction and DSC measurements. Finally we demonstrated dual color LTRM as an application of the difference in the cooling rate dependency of image formation between two different developers.

References

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3. Japanese Patent No. 3113479

Biography

After the career as a researcher on organic photo conductor for 5 years and magnetic recording paper for 3 years, **Ikuo Fujita** is now working on sales and marketing of thermal rewritable recording media (ThermoRewrite).