Evolution and Potential of Thermal Rewritable Marking

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Abstract

The thermal rewritable marking media are now attracting attention because they are useful for the protection of the environment and the indication of information on cards. They may be divided into two types from the principle of rewritable change that are the physical change and the chemical change types. The physical change types may be promising for practical use, because they are high durability and the control of cooling or heating rate for image formation and deletion is not necessary. The image contrast of the chemical change types is excellent due to using leuco dye. The both types are on the market in Japan for the indication of figures on the cards. The development of new application using these media is expected.

Introduction

Materials used as rewritable marking media are now attracting attention from environmental as well as technological viewpoints, because they would converse plastic products such as cards by offering superior functionality, they would find new markets. The rewritable marking is the technology that the images formed by being supplied such energy as heat, light, magnetism, electric field, pressure are maintained without energy supplied and are deleted by being supplied the energy again and can be repeated the image formation and deletion[1].

Photochromic and electrochromic compounds have been objects of study for the rewritable marking media for a long time. Whereas, the photochromic compounds have not used as the recording media because of their light instability. On the other hand, the electrochromic compounds have been applied to a display but have not been used as the recording media, because special devices with electrodes are required.

Over the past few decades, a considerable number of studies have been made on thermal rewritable media due to their stability and development of thermal devices. Thermal rewritable marking media are widely used for the indication of information on cards in Japan. Figure 1 shows examples of the cards using the thermal rewritable marking that we have developed. The opaque images are formed on right two pieces in this figure that are used for loyalty system. In the system, the figures on the cards indicate the value of obtained points in proportion to an amount of paid money for shopping and are rewritten in every shopping. On the other hand, the black images are formed on left three pieces in the figure that will be used widely hereafter due to the high contrast of images. In USA and Europe, the cards using the thermal rewritable marking media do not almost come onto the market, therefore are looked forward to cultivate a market.

This paper deals with the technologies of two kinds of the thermal rewritable media that are on the market, the printing and deleting technologies, and potentialities of these media.

Figure 1. Cards using thermal rewritable marking

Thermal Rewritable Marking Technologies

Table 1 shows the principles of reversible change, materials, and characteristics in the thermal rewritable marking[1]. They may be divided into two types from the principle of rewritable change. The first is the physical changes type that utilized light scattering and color changes by the void change, micro phase separation, change of crystallinity. The second is the chemical changes type that utilized color change by the oxidation-reduction reaction of leuco dye. We will explain the each typical example that is the polymer with dispersed long chain molecules and the leuco dye/long chain developer in the next place. We will also explain the images printing and deleting technology using the thermal rewritable media.

Table 1. Various Thermal Rewritable Marking Technologies.

Principle of reversible change		Materials	Characteristics
Physical change	Void change	Polymer with dispersed long chain molecules	Light scattering change depending on heating temperature
	Micro phase separation	Polymer dispersed liquid crystals	Light scattering change depending on cooling rate
		Polymer blend	
	Change of crystallinity	Liquid crystalline polymer	Light scattering change depending on cooling rate / color change (cholesteric liquid crystalline polymer)
		Cholesteic liquid crystal	Color change depending on heating temperature
		Crystalline polymer	Light scattering change depending on cooling rate
Chemical change	Oxidation-reduction reaction	Leuco dye / long chain developer	Color change depending on heating temperature and cooling rate
		Leuco dye / amphoteric developing / reducing reagent	Color change depending on heating temperature
		Leuco dye / developer / polar organic compound	Colored state at high temperature / decolored state at low temperature
		Leuco dye / developer / steroidal compound	Color change depending on heating temperature and cooling rate

Polymer with Dispersed Long Chain Molecules Type

The thermal rewritable marking media composed of a polymer with dispersed long chain molecules may be promising for practical use, because the two different states (transparent and light-scattering states) can be selected using only temperature, control of the cooling or heating rate is not necessary. The typical examples of the long chain molecules are a fatty acid and a fatty alcohol. That of the polymer is a copolymer of vinyl chloride and vinyl acetate (P(VC-VA)). The long chain molecules are phase separated from the polymer to form small particle domains whose sizes are approximately 1 µm or less.

Figure 2 shows the optical transmittance change as function of temperature in the medium composed of P(VC-VA) with dispersed Behenic acid (BA) on a transparent PET film. When the medium in the light-scattering state (A) is heated to a temperature just below the melting point of BA (80.7 ºC), it becomes transparent (B). This transparency is maintained after the medium is cooled to room temperature (D). On the other hand, when the transparent medium is heated to a temperature above the melting point of BA, it becomes translucent (C) and then reaches the light-scattering state after being cooled to room temperature (A).

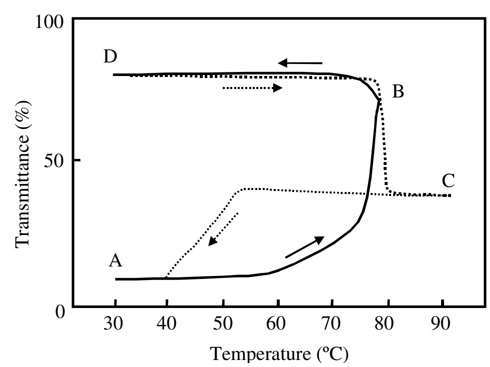

Figure 2. Changes in transmittance during heating and cooling of a media composed of P(VC-VA) with dispersed BA.

The thermal reversible mechanism is illustrated in Figure 3, which shows the structural change of BA particle in the polymer depending on heating-cooling cycle.[2,3] In light-scattering state (A), the domain forms crystals and some voids. The incident light is scattered by the domain because the difference in the refractive index between the air in the voids and the polymer or the BA crystals is very large.

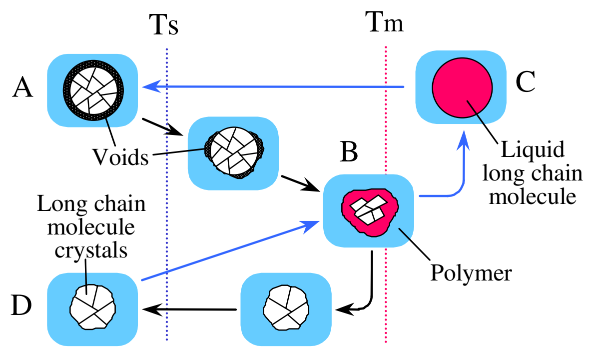

Figure 3. Schematic illustration of internal structural change in the media composed of the polymer with dispersed the long chain molecules in the heating-cooling cycle.

When the light-scattering medium (A) is heated to a temperature just below the melting point of BA (B), the voids decrease and the media becomes transparent above the softening temperature (Ts) of P(VC-VA) and the volume expansion of melted BA fills voids, causing them to disappear. This transparency is maintained after the media is cooled to room temperature (D).

When this transparent medium is heated to a temperature higher than a melting point of BA, BA in the domain melts (C). When the medium is cooled to room temperature, the melted BA in the domain remain a liquid in a supercooled phase until 53 ºC and solidified at about 40-50 ºC to form a group of microcrystals together with many air-filled voids, because the polymer is rigid at the temperature where BA finally crystallize and can not compensate for the volume shrinkage of BA.

The super cooling phenomenon of the long chain molecule greater than 20 ºC which plays a key role in the thermal reversible response of the thermal rewritable media was not shown for the molecules themselves but occurred only when the molecules formed particles dispersed in the polymer.[4]

There were two important points for practical use of this rewritable marking medium. One is the durability of repetition of the image formation and deletion that was improved by a cross-linking of polymer.[5] Another is the image deletion property that was improved by using two long chain molecules having different melting point.

Leuco Dye / Long Chain Developer Type

The rewritable media using a leuco dye have the characteristic that various color images can be formed by a selection of dye.[6] Figure 4a shows the molecular structures of leuco dye that reversibly reveals colored and decolored states by oxidation-reduction reaction. Figure 4b shows examples of the developers having long alkyl chain.

Figure 5 shows the temperature dependence of the optical density of the medium composed of leuco dye and alkyl phosphonic acid.[7] When this medium is heated at state B, they are completely melted and colored. By quenching, the medium is solidified, revealing the colored state C which is maintained at room temperature. On heating from state C, the colored state sharply became decolored at state E and the medium is not colored when the medium is cooled from state E to A even by quenching. Further heating from state E causes the colored state B again. On the other hand, slow cooling from state B results the decolored state A.

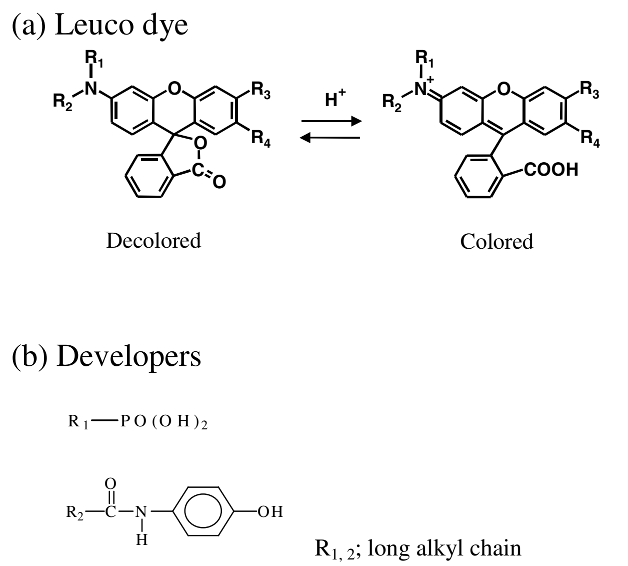

Figure 4. Structures of (a) leuco dye and (b) developer.

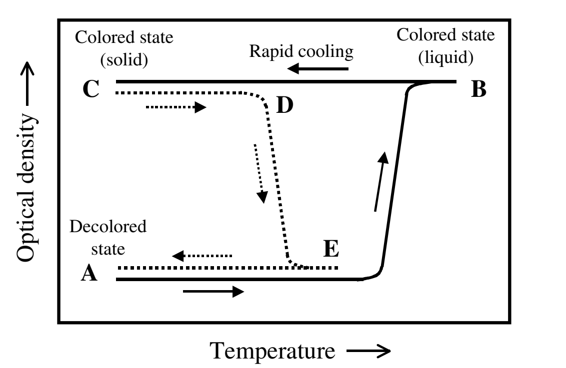

Figure 5. Temperature dependence of optical density of the medium composed of leuco dye and long chain developer.

Figure 6 schematically shows the cyclic reaction of color formation and deletion between the leuco dye and the developer. In the decolored state A, the leuco dyes are separated from the developers that are associated. On heating, both components melt and mix with each other in colored state B. By quenching, the components are solidified and seems to form supramolecule that consist of one molecule of leuco dye and several molecules of developer, forming lamellar structure in state C. On heating state C, the components start to separate (state D) and are kept separate each other in state E. The structure of the components in state E is kept in state A after cooling.

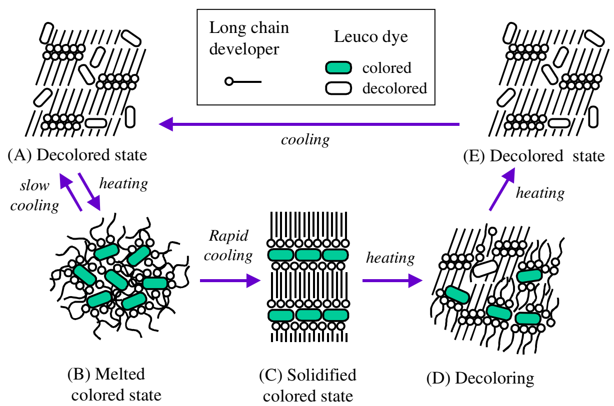

Figure 6. Schematic illustration of internal structural change in the medium composed of the leuco dye and the developer in the heating-cooling cycle.

Printing and Deleting Technologies

The printer for thermal rewritable marking consists of a image formation means and a image deletion means. The thermal print head that is the same as it in the printer for thermal paper is a typical example of image formation means. However, the image deletion means are necessary only for thermal rewritable marking and can be classified into three main groups.[8] The first is a heating roller that can increase the velocity of image deletion but the structure of printer becomes complicated. The second is a ceramic plate heater that is suitable for a card printer due to small and used widely. The third is the thermal print head that is used to printing also, it is called the overwrite marking.[9] This method is that the heat elements in the head are heated on two levels of image formation and deletion temperature.

Laser marking on the thermal rewritable marking media was proposed[10]. The laser marking due to out of contact between the heat source and the medium can obtain the clear image because the marking using the thermal print head has the problem that the images are not formed clearly due to the refuse on the heat elements in the print head.

Potential of Thermal Rewritable Marking

The thermal rewritable marking is useful for the indication on the rewritable memories that are not only the magnetic cards but also IC cards and the rewritable disk. The indication of information on the memories will be a great help for human interface. When the contents in memory are alternated, those of the indications are also changed in corresponding with the alternation of those in the memories and the indications are maintained without any energy. The alternation of memorial contents and the change of the indications can be repeated. The compatibility of rewritable characteristics and memorizable characteristics that maintains the images without any energy could not be achieved in usual displays as CRT and LCD or hard copy made by a copying machine. However, the improvements of the thermal rewritable media and printing/deleting characteristics are necessary for practical application of these new uses.

Summary

The thermal rewritable marking media are expected as one of the high performance media in new application fields in between display and hard copy. Particularly, the media composed of polymer with dispersed long chain molecules and the media composed of leuco dye and long chain developer would become increasingly important in the new fields due to some more excellent properties than the other media, such as no necessity of control of the cooling or heating rate.

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