

Invited Review

Technology and Market of Thermal Rewritable Marking

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Thermal rewritable marking media are now attracting attention because of their low environmental impact and advanced functionality. These media can be divided into two types: media rewritable by a physical mechanism and those rewritable by a chemical mechanism. In Japan, thermal rewritable marking media are now used to store and display information on point cards in consumer loyalty programs. The market for these rewritable marking media is expected to expand with the introduction of new full-color recording material and laser marking technology.

Keywords : Rewritable marking, Long chain molecules, Leuco dye, Long chain developer, Color rewritable, Laser marking

1. Introduction

Rewritable marking media are now attracting attention from environmental as well as technological viewpoints, because they enable conservation of resources such as plastic and offer superior functionality; accordingly, these media are expected to find new markets beyond Japan. Rewritable marking is a technology whereby an image is formed by supplying energy (e. g., heat, light, magnetism, electric field, or pressure) and the image is maintained without energy being supplied. The image can be deleted by again supplying energy, and the process of image formation and deletion can be repeated many times¹⁻³⁾.

Over the past few decades, a considerable number of studies have been conducted on thermal rewritable media, owing to advances in thermal devices and the stability of such media. Thermal rewritable marking media are widely used in Japan to store and display information on point cards used in consumer loyalty programs.

Table 1 shows the principles of reversible change, the materials, and the characteristics of thermal rewritable marking media¹⁾, which can be divided into two types depending on the mechanism of rewriting. The first type utilizes physical mechanisms that lead to light scattering and color change due to void changes, microphase separation, and crystallinity changes. The second type utilizes chemical mechanisms that lead to color change by means of redox reactions of a leuco dye. Each type has different characteristics: physical mechanisms result in images that are resistant to light whereas chemical mechanisms result in images with high

contrast.

2. Progress in the Development of Thermal Rewritable Marking

Developed in 1979 in Germany⁴⁾, the first rewritable marking medium utilized a polymer with dispersed long chain molecules and was based on a physical mechanism. However, this material had the problems of being transparent within only a narrow temperature range and having poor rewriting durability. In 1986, I began to investigate solutions to the problems with this material¹⁾. After that, engineers at multiple companies also started to develop this material. This medium consisting of in a polymer with dispersed long chain molecules was first used commercially as a rewritable marking medium to display information on point cards in 1991³⁾.

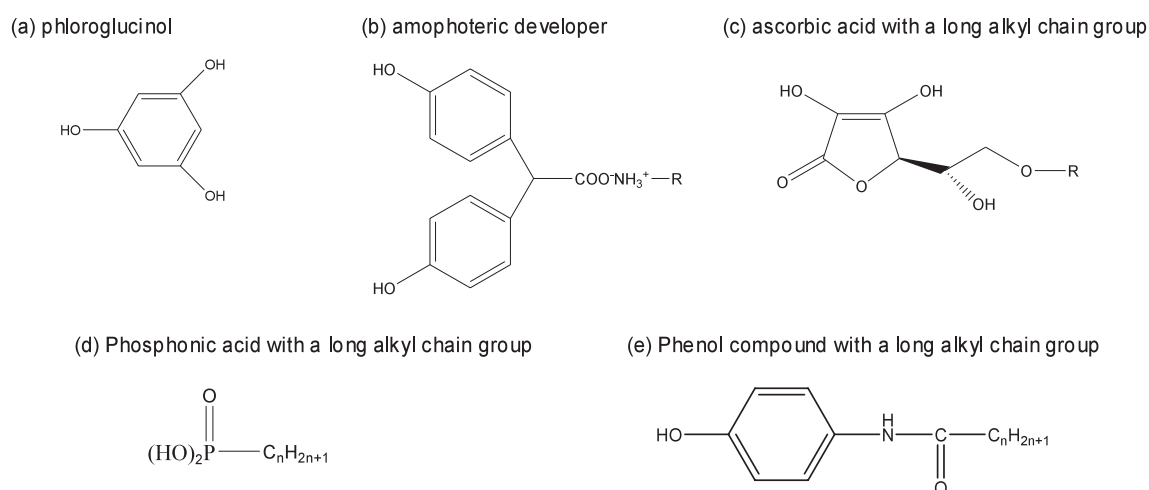
The next type of thermal rewritable marking medium to find practical use was based on a leuco dye. In that technology, which was developed by NCR in the 1960s and widely used until recently, thermal recording paper was colored by the reaction between a leuco dye and developer. However, the color of the thermal recording paper was lost upon contact with grease, plasticizers, and alcohols because the color resulted from a reversible reaction of the leuco dye. This decoloring of the thermal recording paper has been prevented by the development of a new developer and protective layer. The reversible reactions of leuco dyes have been widely utilized in thermal rewritable marking.

Beginning in the 1980s, various methods for thermal rewritable marking have been researched, with focus being placed on the development of new developers. In 1982, Fox of Appleton Paper proposed a rewritable marking medium composed of a leuco dye and phloroglucinol (**Fig. 1(a)**); the

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Table 1 Various thermal rewritable marking technologies¹⁾.

Principle of reversible change	Materials	Characteristics
Physical change	Void change	Polymer with dispersed long chain molecules
	Micro phase separation	Polymer dispersed liquid crystals
		Polymer blend
	Change of crystallinity	Liquid crystalline polymer
		Cholesteric liquid crystal
Chemical change	Crystalline polymer	
	Oxidation-reduction reaction	Leuco dye/long chain developer
		Leuco dye/amphoteric developing/reducing reagent
		Leuco dye/developer/polar organic compound
		Leuco dye/developer/steroidal compound

**Fig. 1** Developers used with leuco dyes for thermal rewritable marking.

medium is colored by heating and decolorized by water vapor⁶⁾. This medium was not put to practical use, however, because of its short shelf life. In 1984, Kitoh of Pilot Ink proposed a rewritable marking medium consisting of a leuco dye, a developer, and a polar organic compound; this medium was decolorized by heating and colored by cooling to less than 0 °C⁷⁾. This medium was put to practical use as pen ink, and friction could erase the image produced with the pen.

In 1990, a thermal rewritable marking was developed that could be rewritten by controlling only the heating temperature. Watanabe of Toppan Printing proposed a rewritable marking medium composed of a leuco dye and the amphoteric developer shown in Fig. 1 (b); this medium was colored by applying heat

for several milliseconds with a thermal printhead and decolorized by the application of heat for several seconds with a hot stamp.

Composed of a leuco dye and a long chain developer, the thermal rewritable marking medium invented by Kubo of Ricoh in 1986 was the first thermal rewritable marking medium based on a chemical mechanism to be put into practical use⁸⁾. Fig. 1 (c), 1 (d), and 1 (e) show examples of the long chain developer^{9,10)}.

In 1997, the thermal rewritable marking medium composed of a leuco dye and a long chain developer was used to display information on point cards. Afterward, the application of the medium was extended to displaying the expiration date on

commuter passes¹¹⁾ and information on “Kanban” cards for process control at factories¹²⁾.

In the following sections, for the two types of thermal rewritable marking media that have found practical use, I will describe the reversible marking mechanism and improvements that enabled practical application of the technology. Specifically, I shall focus on the medium containing a polymer with dispersed long chain molecules, and the medium composed of a leuco dye and a long chain developer. In addition, I shall explain recent trends in thermal rewritable marking, namely, full-color marking and non-contact marking by means of a laser.

3. Polymer with dispersed long chain molecules

The thermal rewritable marking media composed of a polymer with dispersed long chain molecules have the notable characteristic that two different states, transparent and light-scattering, can be achieved by controlling only the heating temperature, regardless of the cooling rate after heating.

The polymer with dispersed long chain molecules exhibit interesting behavior: after being heated to a temperature higher than the melting point, the molecules crystallize at 30°C below the melting point when cooled, whereas after being heated to a temperature just below the melting point, the molecules crystallize at a temperature slightly below the melting point when cooled. The supercooling phenomenon occurs only when the molecules form particles dispersed in the polymer matrix.

Transparent and light-scattering states are controlled in the application of this supercooling phenomenon as shown in **Fig. 2**^{13,14)}. Fig. 2 shows the optical transmittance as a function of temperature and illustrates the structural change of the long chain molecule particles in the polymer, depending on heating-cooling cycle.

When this transparent medium (D) is heated to a temperature higher than a melting point of the molecules, the

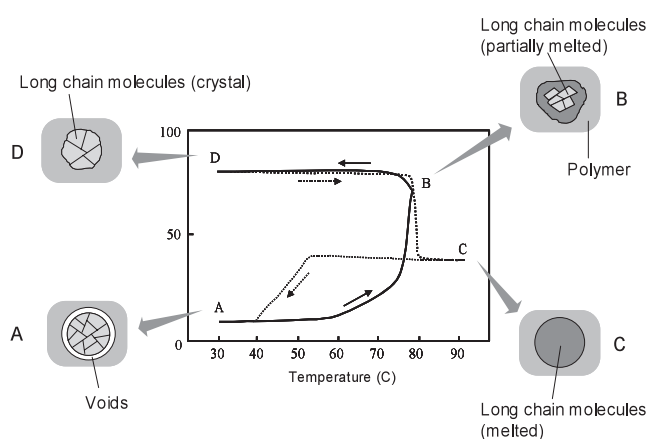


Fig. 2 Thermal reversible mechanism of a polymer with dispersed long chain molecules.

molecules in the polymer matrix melt (C). When the medium is cooled to room temperature, the melted molecules in the matrix remain a liquid in a supercooled state until reaching 50°C. The molecules then solidify at about 40–50°C to form groups of microcrystals together with many air-filled voids, thus causing the medium to change to a light-scattering state (A) because the polymer is rigid below its softening temperature (T_s) and cannot compensate for the reduced volume of the solidified molecules. The hysteresis of over 20°C in the supercooling phenomenon, which plays a key role in the mechanism of thermal rewritable media, is not observed unless the molecules from particles dispersed in the polymer matrix.

When the light-scattering medium (A) is heated to a temperature just below the melting point of the molecules (B), the voids disappear because the volume of the partially melted molecules increases to fill the voids. Therefore, the media becomes transparent (B). This transparency is maintained after the media is cooled to room temperature (D) because the polymer is softened above T_s of the polymer; thus, the polymer can accommodate the volume shrinkage of the molecules without occurrence of supercooling.

Three problems had to be addressed in order to develop this form of rewritable marking medium for practical use.

The first problem was to expand the transparent temperature width. For practical use, a temperature width of 10–20°C is needed to delete the opaque image within 1 or 2 s. Image deletion was improved by using two long chain molecules having different melting points¹⁵⁾.

The second problem was to improve the repetition durability of image formation and deletion to enable several hundred times. It is important to prevent the particle structure of the long-chain molecules from being disrupted by heating and pressure of the thermal printhead. This problem was addressed by moderate cross-link formation in polymer matrix by heating or irradiation of UV with maintaining the softening temperature¹⁶⁾. It was also important to form a hard protective layer on the recording layer¹⁷⁾.

The third problem was to increase image contrast. Fifty percent or more of incident light was transmitted to the opaque recording layer whose thickness was 10–20 μm . The image contrast could be increased by returning the transmitted light to the recording layer by forming a reflective aluminum layer on the back of the recording layer by evaporation coating.

By finding solutions to the above-mentioned problems, thermal rewritable marking media based on a polymer with dispersed long chain molecules were able to be practically used.

4. Leuco dye/long chain developer

Through a change in crystallization, a developer bearing a long alkyl chain group can switch the color state of a leuco dye.

Fig. 3 shows the mechanism of color switching by aggregation and separation of a leuco dye and long chain developer^{18,19}.

Fig. 4 shows the optical density change as a function of temperature and illustrates the structural changes of a composite material consisting of a leuco dye and long chain developer, depending on the heating-cooling cycle. When this material is heated from a solid, colorless state (A) to a temperature above the melting point of the long chain developer, the material becomes colored (B). When this material is quenched from a melted state (B), the leuco dye molecules aggregate while maintaining a bond with the developer, resulting in a stable colored state (C). When the colored material is heated, this aggregate structure collapses (D). The developer returns to an independent crystalline state that is the most stable state and expels the leuco dye, which as a result loses its color (E). This decolorated state (A) is maintained at room temperature.

In the context of this coloring and decoloring process, the intermolecular aggregation force of long chain developers contributes to both the preservation of the colored complex and the phase separation resulting from crystallization.

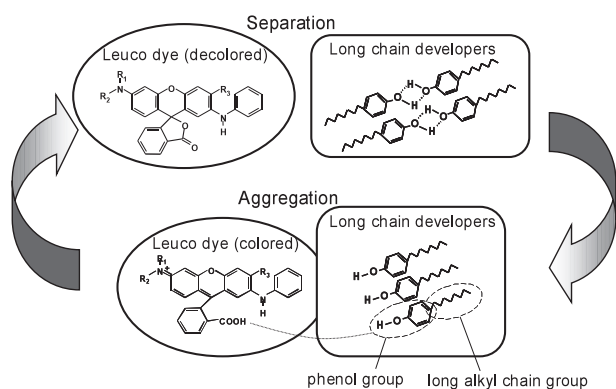


Fig. 3 Reversible color change of aggregate structure of leuco dye and developer.

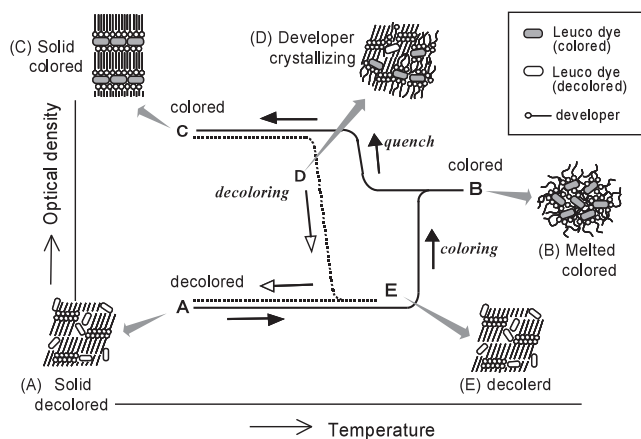


Fig. 4 Thermally reversible mechanism of leuco dye and long chain developer medium.

It was also necessary that three problems be addressed to develop this type of rewritable marking medium for practical use.

Firstly, a balance needed to be struck between the stability of coloring and the rate of decoloring. A strong bond between the leuco dye and developer would improve coloring stability, whereas rapid separation of leuco dye and developer is necessary for high decoloring speeds. The structure of the long chain developer was studied to find an optimal balance²⁰.

Secondly, light-fastness needed to be improved. Leuco dye is broken down easily by light, for example, leading to yellowing of backgrounds and browning of black images on thermal recording paper. It is important to improve the light-fastness of the rewritable medium to allow for long-term use. Forming a UV cut layer on the recording layer was able to address this problem.

Thirdly, the repetition durability of image formation and deletion needed to be improved to allow several hundreds operations, similar to the medium composed of a polymer with dispersed long chain molecules. This problem was addressed by formation of cross-links in the polymer matrix of the recording layer, thus improving the durability to 300 operations or more.

From the results mentioned above, the type of thermal rewritable medium composed of a leuco dye and a long chain developer was able to be successfully used in practical applications.

5. New Trends in Thermal Rewritable Marking

New trends in thermal writable marking are full-color technology and non-contact laser marking.

The first proposed color rewritable medium utilized liquid crystal phase transitions. A cholesteric liquid crystal exhibits intense iridescent colors in the liquid crystal state. These colors arise from the light reflected due to the alignment of the cholesteric molecules in a spatially periodic twisted helical structure. A system has been developed that enables a periodic helical structure of cholesteric molecules to be changed and fixed reversibly, and full-color rewritable recording in various colors can be achieved with a single type of molecule or a single composition. Tamaoki proposed a non-polymeric cholesteric liquid crystal with medium molecular weight (approximately 1000; **Fig. 5**). With this medium, the reflected colors were found to change when controlled at high temperature, and the colors of the marking can be set by rapid cooling²¹. Based on



Fig. 5 Chemical structures of medium molecular weight cholesteric liquid crystal for color rewritable recording.

that finding, the application of this system in rewritable full-color recording materials in thermal mode was proposed.

Another proposal for a color rewritable method is to apply laser recording to the leuco dye/long chain developer system²²⁾. Two advantages of such a method are that various colors can readily be obtained by selection of leuco dyes, and the heated layer can be selected by turning the laser's wavelength. **Fig. 6** shows the principle of a laser-based color rewritable system. The recording medium consists of yellow, magenta, and cyan rewritable recording layers in which various near-infrared dyes are doped. A certain laser wavelength can be used to irradiate a recording layer, and thereby heat each layer individually. Using this system, full-color images on a rewritable recording medium can be accomplished.

We have developed a rewritable system that can form and delete images on a medium composed of leuco dye/long chain developer by means of a high-power laser²³⁻²⁵⁾. **Fig. 7** shows an example of rewritable recording using laser. The image can be formed and deleted in 1 s or less by irradiation of a high-power laser beam (20-30 W) from a distance of 10-20 cm; it is even possible to form images on the medium attached to an item on a conveyor belt, without removing it there from. On the basis of these results, we expect this system to be useful in applications involving physical distribution.

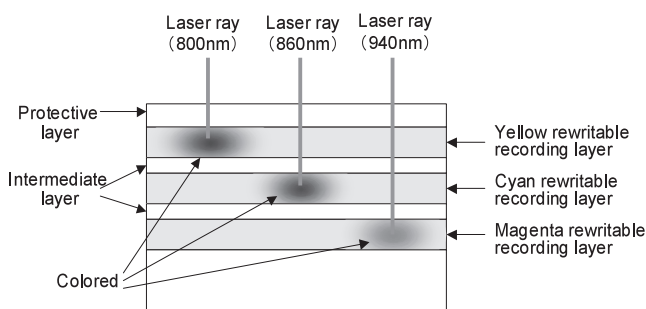


Fig. 6 Color rewritable recording of leuco dye/long-chain developer medium by using lasers with various wavelengths.

6. Summary

Thermal rewritable marking media are on the market in Japan where they are widely used to show information stored on point cards in consumer loyalty programs. An area of future work is spreading this technology to markets other than Japan, and expanding the range of applications beyond point cards. For these purposes, the application of color systems and laser marking technology is expected to be important.

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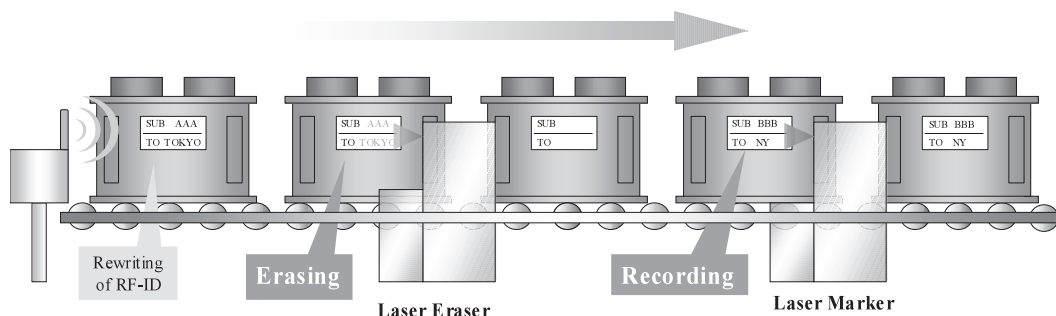


Fig. 7 Example of rewritable marking using a laser for physical distribution.

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