Active Matrix Electronic Paper with Silver Electrodeposition

Noriyuki KOKEGUCHI*, Takeshi HAKII*, Kiyofumi HASHIMOTO*

Abstract

In recent years, many technologies relating to electronic paper and related products have been developed or proposed. But the gulf between the quality of electronic paper so far achieved and the merits of standard paper still exists. Many technological problems are yet to be solved, and we chose to focus on improving the display quality of electronic paper documents, which is very important to document readability. We developed a 3.5 inch sheet of electronic paper, driven by an active-matrix using silver electrodeposition, and, for an electronic paper, exhibiting the highest level of whiteness in the world. The electronic paper has a white reflectivity of over 60%, approaching that of copy paper, and a contrast ratio of at least 20:1, which together realize visibility equivalent to copy paper.

1 Introduction

An electronic paper is expected as a medium of the next generation which has strong points of both paper and a display. That is, visibility of paper, and re-writability of display. In order to realize the electronic paper, various technologies have been known, such as, Ch-LCD (Cholesteric-LCD), PN-LCD (Polymer Network LCD), a reflective LCD, and an electrophoretic display. But quality levels of these technologies have not met the customer satisfaction (Fig. 1).

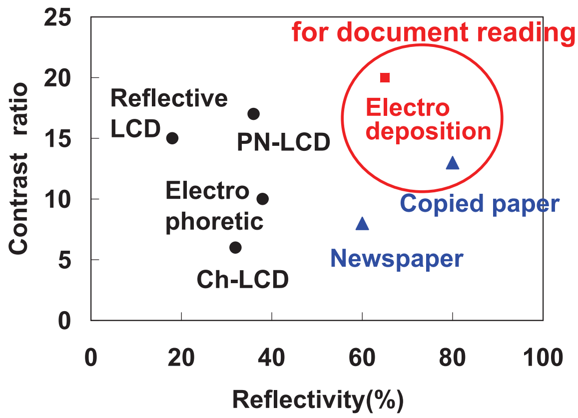


Fig.1 Reflectivity vs. contrast ratio of various media

As a display type electronic paper, technical development of the electrophoretic method and the Ch-LCD method has preceded, but the reflectivity of white state has been at most 40% and less than the whiteness of paper (60% or more). On the other hand, electrochemical methods could theoretically realize a high reflectivity and a high contrast. Among these methods, an electrodeposition method exhibited an excellent display potential [1~3], but they were using passive-matrix drive, and the method had various problems to be solved for use as a device for document readings, for instance, driving stability, a gray color tone and bi-stability. The active-matrix device using electrochromic dyes has

*Device Technology R&D Laboratories
KONICA MINOLTA TECHNOLOGY CENTER, INC

been known [4], but this device has showed blue images against white background, therefore, a black and white display which is important for a document reading was not realized. We will report that the above-described performance of the display has been improved by development of a new halogen-free silver salt electrolyte composition and a porous-white scattering layer, and a black and white electronic paper driven by 3.5 inch active-matrix using the silver electrodeposition has been developed.

2 Novel Display Structure and Mechanism

Fig. 2 shows a display structure of our silver electrodeposition display. A porous-white scattering layer is sandwiched between a pair of electrodes, and this layer incorporates silver salt electrolyte solution. We used silver in this electorodepsion display, because deposited silver exhibits pitch black, and further, because a silver ion is monovalent. On the other hand, a bismuth ion is trivalent. So the electric power consumption of silver is one-third of that of bismuth. The coloring mechanism is as follows. A silver atom and a silver ion are reversibly changed by applying voltage of within one point five volt. By an oxidation-reduction reaction at an electrode interface, appearances of black and white states are reversibly changed. The black state appears when the silver is deposited, and the white state appears when the silver is dissolved in electrolyte.

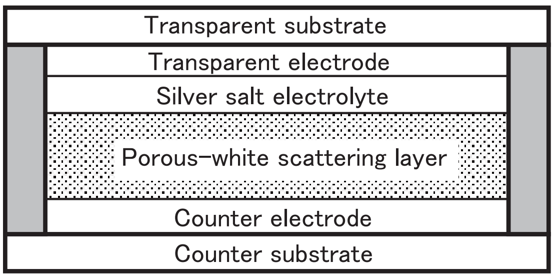


Fig.2 Schematic cross-sectional view of silver electrodeposition display

3 Porous-White Scattering Layer

Fig. 3 shows a sectional view of porous-white scattering layer we developed. We have achieved the highest and constant whiteness of a display with minimum amounts of titanium dioxide. The layer consists of particles of titanium dioxides (TiO_2) covered with polyvinyl alcohol, and has a porous form so that silver salt electrolyte can permeate into it. Polyvinyl alcohol plays a role of fixing the particles of TiO_2, and does not dissolve in the silver salts electrolyte.

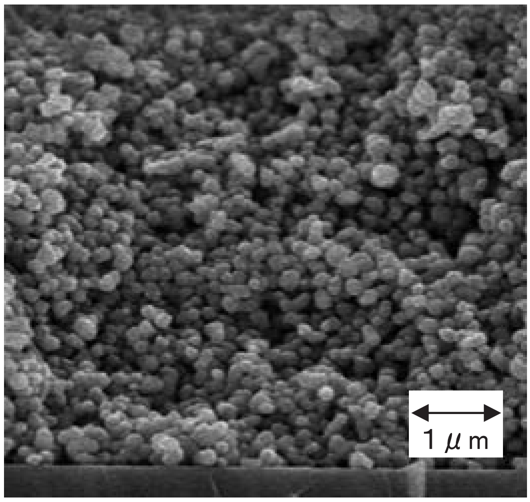


Fig.3 Sectional view of a porous-white scattering layer

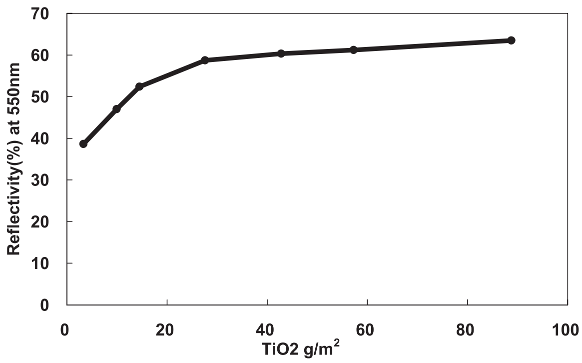
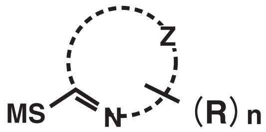


Fig.4 Reflectivity vs. amount of TiO_2

Fig. 4 shows a relationship between the amount of titanium dioxide and reflectivity at five hundred and fifty nanometers. Reflectivity increases sharply up to the amount of thirty grams per square meter, and is mostly saturated in the region over the amount. The porous-white particles are made using the amount of titanium dioxide of this flat region. So, even if the amount of titanium dioxide varies a little in a manufacturing process, the change of reflectivity is slight. The porous-white scattering layer plays an important role. When a white pigment is incorporated in the electrolyte liquid, the dispersion of the white pigment is not fully stable, and then the reflectivity varies with time. In this case, however, such a reflectivity change does not occur, because the titanium dioxide is fixed. And because minute filling of the titanium dioxide is carried out, this system gives the highest whiteness per unit cross-section area compared to other types of electronic paper.

4 New Halogen-Free Silver Salt Electrolyte

Formula 1 shows a general formula of the newly developed silver salt solvent. In Formula 1, M represents a hydrogen atom, a metal atom or a quarternary ammonium; Z represents a group of atoms necessary to form a nitrogen containing heterocycle combined with a carbon atom and a nitrogen atom; n represents an integer from 0 to 5; and R represents a hydrogen atom or a substituent. Table 1 shows a comparison of the electrolyte compositions. In order to dissolve silver, a silver halide or an alkali halide had been used. By having developed these compounds, it became possible to remove a halogenated compound from silver salt electrolyte to result in enhanced performances of gray color tone, driving stability and bi-stability as a display.



Formula 1: Newly developed silver salts solvents

Table 1 Comparison of electrolyte composition

	Electrolyte 1 (previous work)	Electrolyte 2 (present work)
Solvent	DMSO	PC
Silver salt	silver iodide	silver p-toluene-sulfonate
Silver salt solvent	sodium iodide	mercapt-azole (Formula 1)

5 Reflectivity and Gray Color Tone

Fig. 5 shows reflection spectra of electrolyte 2 when 1.5 V was applied between a pair of electrodes with changes of the applied time. It has reflectivity of at least 60%, and contrast ratio of at least 20 or more. Moreover, the forms of the visible portion of the reflection spectra are mostly flat, resulting in an excellent gray color tone.

Fig. 6 shows reflection spectra of electrolyte 1 at the same condition as the electrolyte 2. The forms of the visible portion of the reflection spectra are not flat, leading to a dark reddish-brown color tone.

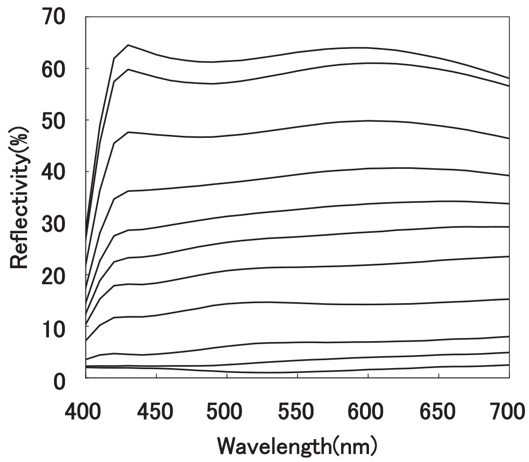


Fig.5 Reflection spectrum dependence on applied time (electrolyte 2)

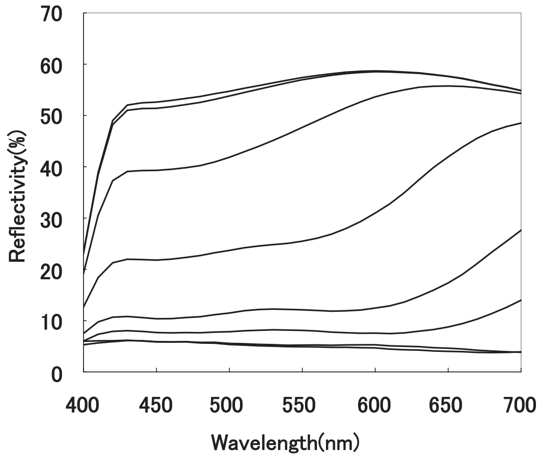


Fig.6 Reflection spectrum dependence on applied time (electrolyte 1)

When a silver salt electrolyte composition is changed, the color tone of deposit silver will change. It is presumed that the difference in a color tone relates to the size of the particles of deposit silver. In the case of the electrolyte 2, the mercapto group effectively controls the size. For a black and white electronic paper, electrolyte 2 is superior to electrolyte 1

6 Bi-stability

Fig. 7 shows a cyclic voltammogram for the silver redox reaction. A peak accompanying silver reduction (black state) is observed at the lower left. Another peak accompanying silver oxidization (white state) is observed at the upper right. The reproducibility of a driving repetition was excellent. As the peak shape shows the hysteresis, this electrodeposition display has bi-stability

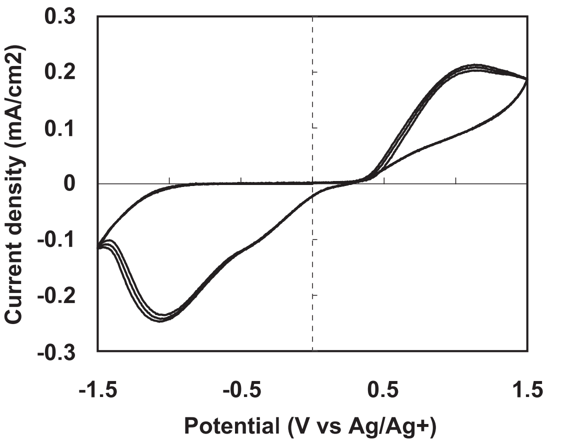


Fig.7 Cyclic voltammogram for the silver redox reaction

Fig. 8 shows an evaluation result of bi-stability. The horizontal axis shows an amount of change from 10% of reflectivity per minute measured with a circuit between opposing electrodes open. The bi-stability of an electrolyte 2 was also improved by about 10 times compared to the electrolyte 1. Therefore, the removal of halogen from the electrolyte sharply improved the bi-stability. The improvement in bi-stability is a very important element for the stable drive of this electro-deposition display.

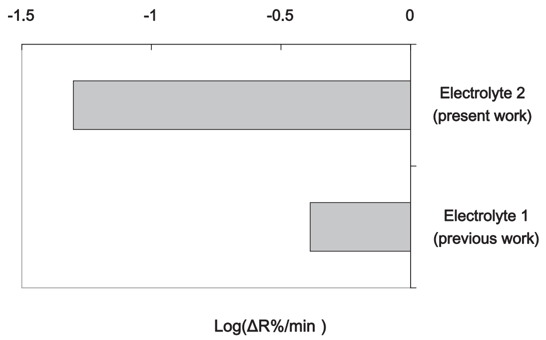


Fig.8 Bi-stability increase by removing halogen from electrolyte

7 Prototype Active Matrix Driving

Fig. 9 shows prototypes of our electronic paper (3.5 inch & 113 ppi) with an active-matrix drive using the newly developed electrolyte. The prototypes are composed of a back plane (LTPS-TFT), a porous-white scattering layer, silver salt electrolyte, a transparent electrode, and a transparent substrate. The silver salt electrolyte can penetrate into the porous-white scattering layer. Between the pair of opposed electrodes, voltage of -1.5 (black state) or +1.5 (white state) is applied. In figure 9, a sheet of copied paper is under the prototypes. The reflectivity is 63% and the contrast ratio is 20 or more, and then visibility equivalent to copied paper is realized. The features of the prototypes are summarized in Table 2.

Table 2 Display characteristics

White state reflectivity	63 %
Contrast ratio	> 20
Driving voltage	1.5 V
Size	3.5 inch
Resolution	113 ppi
Drive	LTPS-TFTs

Fig.9 Images of electronic paper (3.5 inch & 113 ppi) with silver electrodeposition driven by LTPS-TFTs

Fig.10 Image of the prototype when viewed nearly end-on

Fig.11 Image of the prototype compared with a newspaper

Fig. 10 shows an image of the prototype when viewed nearly end-on. Visibility is good even if viewed from a different angle from at right angle. Fig. 11 shows an image of the prototype compared with a newspaper. The reflectivity of the white state is at most 20% brighter than a newspaper.

8 Conclusion

An electronic paper of 3.5 inch with an active-matrix drive using the silver electrodeposition has been developed. By having developed a new halogen-free silver salt electrolyte composition, driving stability, a gray color tone, and bi-stability have been considerably improved, and having developed porous-white scattering layer structure, excellent properties (reflectivity of at least 60%, and contrast ratio of at least 20) realized visibility equivalent to paper. So this device can display images with the highest whiteness and contrast as an electronic paper. We are going to decrease the response time, develop a device having a large area, and increase the durability.

References

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(An additional note: The contents described in this paper was presented at Society for Information Display 2008 International Symposium (Digest of technical papers Vol.39,p.1022))