Fabrication of the Plasma-Chemical Indicator and It’s Application

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In order to confirm the plasma processing effect at a required point by visual observation, the plasma-chemical indicator (PCI) was fabricated. In this research, the effects of NC and PA on discoloration properties of PCI was examined, since the color of prepared printing ink was fairly affected by the kind of binder. Viscosity effects of these binders on the sensitivity of PCI were also investigated. As an Application of PCI, the 3D mapping was created by the color difference \( \Delta E_{ab} \) obtained by 15 min of H\_2\_O plasma irradiation using 25 pieces of PCI.

It was found that the influence of viscosity on change of color is small, comparing with the influence by the kind of binder. The expansion effect of an indicator range was able to be confirmed for H\_2\_O and H\_2\_O\_2 plasma, but not for O\_2 plasma. The optimal mixing ratio of NC and PA for H\_2\_O and H\_2\_O\_2 plasma was 5 and 15 wt/wt, respectively. 3D mapping which visualized the situation was well in agreement with the visual observation results.

Keywords: Plasma-chemical indicator, Discoloration, H\_2\_O plasma, H\_2\_O\_2 plasma, O\_2 plasma.

1. Introduction

The plasma-chemical indicator (PCI) is the piece of PET (polyethylene terephthalate) sheet strip on which a color indication mark is printed using ink which discolors by the plasma chemical action. The aim of PCI is to confirm the plasma processing effect at a required point in situ by visual observation.

In the previous report [1], PCI of sensitive and distinguishable to 30% H\_2\_O\_2 and O\_2 plasma was fabricated by screen printing on a PET sheet using printing ink prepared on the bases of composition of ordinary gravure ink in which two different colorants, red azo-dye (Az-R) and green phthalocyanine pigment (Ph-G) and nitro cellulose (NC) and polyamide (PA) resins as binder were used. When PCI was treated by H\_2\_O and H\_2\_O plasma, the color continuously shifted from the purple of control PCI toward dull light green and light bluish green respectively during 15 minutes of treatment time by the action of \( \cdot \)OH formed. While, when the PCI is treated by O\_2 plasma, it also continuously shifted toward a pinkish color during 15 minutes of treatment time by the action of O\_2(\(^1\Delta_g\)) as shown in Figure 1. Therefore, it could be said that this prepared PCI is sensitive and distinguishable from H\_2\_O\_2 or H\_2\_O and O\_2 plasma.

In this research, in order to optimize the ink composition, we examined the effects of NC and PA on discoloration properties of PCI, since the color of prepared printing ink was fairly affected by the kind of binder. Viscosity effects of these binders on the sensitivity of PCI were also investigated.

We also found in the previous report [1] that the ordering of weight loss (wt%) in Az-R and Ph-G was H\_2\_O plasma > 30% H\_2\_O\_2 plasma for both colorants. This suggests that the number of \( \cdot \)OH formed is larger in H\_2\_O plasma than in H\_2\_O\_2 plasma.
plasma. Considering the dissociation energy of OH in H₂O (498.2 kJ/mol) and O-O in H₂O₂ (213.5 kJ/mol) [2], ·OH seems to be easier to form in H₂O₂ plasma than in H₂O plasma. In order to confirm the above tendency obtained by a weight loss measurement experiment, the experiment using PCI as a sensor of ·OH concentration was examined.

2. Experimental

2.1. Materials

As for colorants, Red azo-dye (C. I. Solvent Red 167:1, Az-R) and green phthalocyanine (C. I. Pigment Green 7, Ph-G) were used similarly to the previous report [1]. Characteristics of nitrocellulose (NC) supplied from CHYMIA and polyamide (PA) of Versamid Series supplied from BASF used in this experiment were summarized in Tables 1 and 2, respectively. Cyclohexanone and 2-n-butoxyethanol with chemical grade supplied from Kanto Kagaku were used as solvent. Cationic surfactant of quaternary ammonium salt (alkyltrimethylammonium chloride) supplied from Nikko Chemical was used as dispersant.

Crisper® supplied from TOYOBO was used as PET sheet for the PCI substrate.

2.2. Preparation of PCI

PCI was fabricated by screen-printing on a PET sheet using printing ink prepared according to the recipe listed in Table 3. The printing ink was prepared using the laboratory mixer ROBOMIX®. The printed PET sheet was cut into 2 × 8 cm strips.

2.3. Plasma Irradiation Experiment

Plasma treatment of PCI with different plasma gas source was carried out in the same manner as described elsewhere in our previous report [1] using the same bell-jar type of plasma reactor (Samco).

<table>
<thead>
<tr>
<th>Grade</th>
<th>Soft. Point (°C)</th>
<th>Viscosity in Melt @160 (mPa·s)</th>
<th>Viscosity in Soln. (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS 1/2</td>
<td>110-120</td>
<td>300-500*</td>
<td></td>
</tr>
<tr>
<td>RS 7</td>
<td>105-115</td>
<td>2,11-2,700</td>
<td>120</td>
</tr>
<tr>
<td>SS 1/2</td>
<td>93-103</td>
<td>2,500-3,000</td>
<td>152</td>
</tr>
</tbody>
</table>

*: @120, **: @190

Table 3. Recipe of the printing ink for PCI.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Contents (wt/wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexanone</td>
<td>14.7</td>
</tr>
<tr>
<td>2-n-butoxyethanol</td>
<td>57.0</td>
</tr>
<tr>
<td>Az-R</td>
<td>0.3</td>
</tr>
<tr>
<td>Ph-G</td>
<td>1.0</td>
</tr>
<tr>
<td>PA</td>
<td>5.0-10.0</td>
</tr>
<tr>
<td>NC</td>
<td>5.0-10.0</td>
</tr>
<tr>
<td>Surfactant</td>
<td>2.0</td>
</tr>
<tr>
<td>Silica</td>
<td>10.0</td>
</tr>
</tbody>
</table>

The reactor was equipped with an 8.8-L bell-jar in which parallel disk-electrodes were set. Plasma gas was introduced downward like a shower from the upper electrode. The lower electrode is equipped with rotatable magnet inside so that uniform treatment with condensed plasma around the electrode could be obtained. Liquid plasma sources such as H₂O₂ and H₂O were supplied from 50 mL glass ampoule kept at a steady temperature of 50°C and steady plasma gas flow was maintained using a needle valve and ultrasonic
irradiation during treatment. These connecting lines made of stainless steel pipe were kept warm enough to prevent coagulation of these liquid sources. PCI was placed on the lower electrode, and then H₂O₂, H₂O and O₂ plasma treatment was carried out at a fixed plasma gas flow rate and rf power of 2.0 mmol/min and 75 W, respectively for given periods of time. Although the pressure of the system was governed by the flow rate of the plasma gas source, it was about 40 Pa when the plasma was not generated. Oxygen flow rate and rf power was controlled by mass flow controller (STEC) and rf (13.56 MHz) generator (ADTEC, AX-1000).

2.4. Measurements
2.4.1. Discoloration
Discoloration of PCI specimens after plasma treatment were compared using the CIELAB color indicating system obtained from reflectance measurements results measured by color analyzer TC-1800 manufactured by Tokyo Denshoku. In CIELAB system, the L* axis represents the lightness (L* varies from 100 (for white) to 0 (for black), and a* and b* are the chromaticity coordinates (+a* is for red, -a* for green, +b* for yellow, -b* for blue). L*, a* and b* values were used to calculate the overall color differences ΔE*ab using the following equation:

\[ \Delta E^{*ab} = \left[ (\Delta L^{*})^2 + (\Delta a^{*})^2 + (\Delta b^{*})^2 \right]^{1/2} \]  

(1)

Where ΔL*, Δa* and Δb* are the difference of initial and final value (before and after plasma treatment) of L*, a* and b*, respectively.

2.4.2. Emission Spectroscopy
Emission strength at 778 nm attributed to •OH [3] was measured using UV-VIS monochrometer (Shimadzu, SPG-120S) and optical power meter (Advantest, TQ-8210).

3. Results and Discussion
3.1. PCI with single binder
At the beginning, we examined PCI using ink prepared by single binder, NC (NC-PCI) or PA (PA-PCI), according to the recipe shown in Table 2. In this case amounts of NC or PA were fixed to 15 wt/wt, respectively.

Figures 2 and 3 show the relationship between plasma treatment time and color change expressed by a* and b* in CIELAB when NC-PCI and PA-PCI are irradiated by H₂O₂ plasma for 0, 1, 3, 5 and 10 min, respectively. In NC-PCI, it was found that the starting color varies somewhat and located at the position of medium-rise right in the (+a*, -b*) quadrant, appeared purple with average color coordinates of (11, -7). When H₂O₂ plasma is applied, it shifted in the direction of the upper left of a graph, and has gathered near the upper right of (-a*, -b*) quadrant in 10 minutes, appeared nearly colorless with average color coordinates of (-2.5, -2.5). The influence of viscosity on color change was slight.

On the other hand, in PA-PCI, the starting color located at the position of medium-rise left in the (+a*, -b*) quadrant, appeared strong blue with average color coordinates of (5, -8).
When H₂O₂ plasma was applied, it turns out that it shifted in the direction of the upper left of a graph, and gathered near the upper center to left of the (-a*, -b*) quadrant in 10 minutes, appeared green with average color coordinates of (-9, -4). It could be said that the influence of viscosity on change of color is small, comparing with the influence by the kind of binder.

Thus, since the color of PCI was extremely dependent on the kind of resin throughout 10 minutes of plasma irradiation, it was expected that mixing these two kinds of resin would lead to the expansion of an indicator range. That is, mixing NC and PA resins will exist as one of the means of an indicator range expansion, that can lead to the development of the PCI with higher resolution.

Next, NC and PA were mixed and the expansion effect of the indicator range was confirmed. The result obtained by H₂O plasma as an example is shown in Figure 4.

![Figure 4](image-url)  
**Figure 4.** The indicator range of PCI in which NC (RS1/2) and PA (335) are mixed by 5 wt/wt and 15 wt/wt, respectively.

It was confirmed from Figure 4 that PCI showed improved discoloration performance against -OH reaction brought by H₂O or H₂O₂ plasma and an indicator range beyond the indicator ranges of NC-PCI and PA-PCI by mixing NC and PA.

Figures 5 and 6 show the relationship between plasma treatment time and color change expressed by a* and b* in CIELAB when NC-PCI and PA-PCI are irradiated by O₂ plasma for 0, 1, 3, 5 and 10 min, respectively.

![Figure 5](image-url)  
**Figure 5** The relationship between O₂ plasma treatment time and color change in NC-PCI.

![Figure 6](image-url)  
**Figure 6** The relationship between O₂ plasma treatment time and color change in PA-PCI.

Although the starting colors differ by NC-PCI and PA-PCI, when O₂ plasma was applied, it shifted in the direction of the upper left during 1 to 3 min from the start, after that, it immediately shifted to the upper rightist side of (+a*, -b*) quadrant, then appeared pink as a terminal color after 10 min from the start with the average color coordinates of (20, -3). This profile was alike in both PCI. As for the shifting in the direction of the upper left during 1 to 3 min from the start, this seems to be due to the decomposition of red Az-R existing in the surface layer of the ink film.
Therefore, with oxygen plasma, the decomposition and etching of the surface layer of the ink film in which Az-R dye is dissolved seems to be progressed. After that, when the green Ph-G particles hidden into the ink film begin to appear, their decomposition became dominant.

In the case of O₂ plasma, it could be said that the influence of viscosity on change of color is small, comparing with the influence by the kind of binder.

Next, NC and PA were mixed and the expansion effect of the indicator range was confirmed. The result obtained by O₂ plasma is shown in Figure 7.

![Figure 7](image)

Figure 7. The indicator range of PCI in which NC (RS1/2) and PA (335) are mixed by 5 wt/wt and 15 wt/wt, respectively.

As seen in Figure 7, the expansion effect of an indicator range was not able to be confirmed. The value of +a* was small and it turned out that red coloring was suppressed as a result.

As though the expansion effect of an indicator range was not able to be confirmed against O₂ plasma, optimum mixing rate of NC and PA for H₂O and H₂O₂ plasma were found to be 5 wt/wt and 15 wt/wt, respectively. Then we refer to PCI with mixed binder of 5 wt/wt NC and 15 wt/wt PA as PV-PCI, Prototype Version PCI, for convenience.

### 3.2. Resolution of PV-PCI

As described above, we found that the ordering of weight loss (wt%) in Az-R and Ph-G was H₂O plasma > 30% H₂O₂ plasma for both colorants. It suggesting that in the number of ·OH generated, H₂O plasma exceeds rather than 30% H₂O₂ plasma.

In order to confirm the result obtained by weight loss measurement experiment, ·OH concentration in the plasma emerged by H₂O₂ aqueous solution with different concentration was investigated by PV-PCI.

Figure 8 shows the relationship between concentration of H₂O₂ and color differences ΔE*ab when PV-PCI are irradiated for 15min by respective plasma with different H₂O₂ concentrations.

It was found that the color difference ΔE*ab linearly decreased with increasing concentration of H₂O₂. This result indicates that ·OH concentration in H₂O₂ plasma is higher than in 30% H₂O₂ plasma. In order to confirm this tendency, ·OH concentration was measured spectroscopically, by measuring the emission strength at 778 nm attributed to ·OH.

![Figure 8](image)

Figure 8. The relationship between concentration of H₂O₂ and color differences ΔE*ab when PV-PCI are irradiated by respective plasma for 15min.

Figure 9 shows the relationship between input power and emission strength at 778 nm for H₂O plasma and 30% H₂O₂ plasma with a steady plasma gas flow rate of 2.0 mmol/min, respectively. Since the experiment was conducted by uniting the number of molecules of a plasma gas supplied, energy density per unit number of plasma gas molecules is equal.

It was found that that emission strength at 778 nm linearly increased with increasing input power in both H₂O plasma and 30% H₂O₂ plasma, and 0.1402 and 0.1199 were obtained as inclination, respectively. That is, ·OH concentration in H₂O plasma could be said to be 1.17 times greater than in H₂O₂ plasma. This result showed very good concurrence for the former results [1] of the decomposition experiment of colorant by the H₂O and H₂O₂ plasma.
Figure 9. The relationship between input power and emission strength at 778 nm for H$_2$O and H$_2$O$_2$ plasma with a steady plasma source flow rate of 5.0 mmol/min.

About the lowness of ·OH concentration in plasma state 30% H$_2$O$_2$ having relatively low dissociation energy of O-O, it is considered for an electron to receive repulsion by the high electronegativity of both two O elements.

From the above result, it could be said that PV-PCI has resolution which can distinguish enough ·OH concentration difference in H$_2$O and 30% H$_2$O$_2$ plasma. Judging from visual observation of PCI, it seems that distinction of H$_2$O and 15% H$_2$O$_2$ plasma is also possible.

3.3. Application of PV-PCI

For the Application of PV-PCI, the plasma processing effect at a required point was visualized. The action of the H$_2$O plasma near the lower electrode of diameter 10 cm which was visualized by 3D mapping and described in Figure 10. In Figure 10, the 3D mapping was created by the color difference $\Delta E^*_{ab}$ obtained by 15 min of H$_2$O plasma irradiation using 25 pieces of PCI arranged on the surface of Pyrex plate (100 $\times$ 100 mm), which was placed on the lower electrode. As for the density of plasma during plasma irradiation, it was observed that luminescence near the electrode of the central part was weaker than the circumference. 3D mapping which visualized the situation was well in agreement with the visual observation results.

4. Conclusion

It was found that the influence of viscosity on change of color is small, comparing with the influence by the kind of binder.

The expansion effect of an indicator range was able to be confirmed for H$_2$O and H$_2$O$_2$ plasma, but not for O$_2$ plasma. The optimal mixing ratio of NC and PA for H$_2$O and H$_2$O$_2$ plasma was 5 and 15 wt/wt, respectively. Judging from the relationship between concentration of H$_2$O$_2$ and color differences $\Delta E^*_{ab}$, it was found that the color difference $\Delta E^*_{ab}$ linearly decreased with increasing concentration of H$_2$O$_2$, and clarified that ·OH concentration in H$_2$O$_2$ plasma is higher than in 30% H$_2$O$_2$ plasma. This result agreed well with the results obtained by the spectroscopic measurement. For the Application of PV-PCI, 3D mapping was created by the color difference $\Delta E^*_{ab}$ obtained by 15 min of H$_2$O plasma irradiation using 25 pieces of PCI arranged on the surface of Pyrex plate. 3D mapping which visualized the situation was well in agreement with the observation results.

References

2. Handbook of Chemistry and Physics, 72nd Ed., CRC.