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TECHNICAL NOTE

COBALT-FREE HUMIDITY INDICATOR CARD BASED ON ORGANIC DYES

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ABSTRACT

Since International Agency for Research on Cancer (IARC) determined that cobalt (II) chloride is carcinogenic to human, cobalt-free humidity indicators have attracted considerable attention. The composites of polystyrene sulfonic acid (PSS) with various organic dyes based on organic dyes were coated on a polyethylene terephthalate (PET) film. The coated film exhibited color change depending on humidity. The change of color was evaluated by using L*a*b* coordinates. Further, addition of hygroscopic inorganic salt such as magnesium chloride was found to be effective in tuning humidity range.

KEYWORDS

Chloride, cobalt-free humidity, polystyrene sulfonic acid, polyethylene terephthalate.

1. INTRODUCTION

A humidity indicator card (HIC) is a card on which a moisture-sensitive chemical is impregnated such that it will change colour when the indicated relative humidity (RH) is exceeded. This is usually blotting paper impregnated with cobalt(II) chloride. This item is an inexpensive way to quantify relative humidity levels inside sealed packaging. They are available in many configurations and used in many applications such as semiconductors and electronic devices. The most common HIC is based on cobalt(II) chloride and its colour changes from blue (less than indicated RH level) to pink (greater than indicated RH level). Since International Agency for Research on Cancer (IARC) determined that cobalt(II) chloride is carcinogenic to human, cobalt-free humidity indicators have attracted considerable attention (WHO, 1991).

A number of cobalt-free humidity indicators have been developed and some of them were already commercialized (Fueda et al., 2007; Oe et al., 2002). However, there still remains room for improvement. These materials have showed only small colour change between dry and humid conditions compared with CoCl2-based materials. Several approaches have been investigated to propose new materials for cobalt-free humidity indicators. These include silica gel impregnated iron (III) salts, sugar gels containing ionic dyes, porphyrin/$MgCl_2$/silica gel composite, inorganic polymers (geopolymers) containing acid-base indicator, hydroxyethyl cellulose containing methylene blue and urea, and composite of polyvinyl alcohol with sodium borate decahydrate (Moreton, 2002; Matsushima et al., 2003; Matsushima et al., 2000; Matsushima et al., 2002; Fueda et al., 2007; Matsumoto et al., 2011; Mackenzie and O'Leary, 2009; Mills et al., 2010; Mujahid et al., 2012).

Recently, Ichikawa et al. reported reversible colour change of binary films composed of azobenzene containing triphenyl amine and p-toluene sulfonic acid in response to exhaled breath, indicating that combination of organic acid and organic dye (pH indicator) will be a s promising material for cobalt-free HIC (Ichikawa et al., 2015). Thus, we examined materials composed of polystyrene sulfonic acid (PSS) and organic dyes. The reason of our choice of PSS as an organic acid compound is its fabrication ability on a plastic sheet. In this paper will be reported new humidity indicator composed of PSS with various organic dyes and the observed colour changes were evaluated by L*a*b* colour space. Further, addition of hygroscopic inorganic salt such as magnesium chloride was found to be effective in tuning humidity range.

2. METHODOLOGY

2.1 Materials

Sodium polystyrene sulfonate and acid cation exchange resin, DOWEX HCR-W2, were purchased from Wako Pure Chemical Industries, Ltd. Four organic dyes such as crystal violet (CV), brilliant blue FCF (BB), bromothymol blue (BTB), and neutral red (NR) were purchased from Aldrich. Magnesium chloride was purchased from Kanto Chemical Co., Inc. Toray Lumirror S10 (thickness, 50 μm) was used as a base film.

2.2 Polystyrene sulfonic acid (PSS)

Into a solution of sodium polystyrene sulfonic acid (4.0 g) in 80 mL of water was added Dowex HCR- W2 (10 g) and the mixture was stirred for 3 h at room temperature. The mixture was filtered and evaporated to give 3.4 g (95%) of PSS as an amber solid. IR (KBr): ν = 1220 (s), 1177 (s), 617 cm^{-1} (m); ^1H NMR (500 MHz, D_2O, δ): 7.7-7.3 (m, 2H), 6.8-6.3 (m, 2H), 1.8-1.2 (m, 3H).

2.3 General preparation procedure of fabrication

A mixture of PSS (0.55 g) in 10 mL of water, 0.1 mmol of dye in 5 mL of ethanol, and a given amount of aqueous solution of inorganic salt (0.25 mol/L), if necessary, was stirred at room temperature under ultrasonication for 3 min. The solution was coated on a PET film using bar coater (YASUDA SEIKI, RD20) and dried at 100 °C for 15 min.

2.4 Measurements

The desired relative humidity level (from 10% to 90%) was achieved by placing an aqueous glycerin solution in the glass chamber at 25 °C. Color was measured by Konica-Minolta CR-13 color reader. The illumination angle and illuminant were 8° and CIE illuminant D65, respectively. The obtained color difference data were analyzed with Δ(L*a*b*), where L* stands for luminance, a* is the red- green axis, and b* is the blue-yellow axis. These values can make it possible to obtain an objective and quantifiable assessment of the color.

3. RESULTS AND DISCUSSION

The chemical structures of four organic dyes examined in this study are shown in Figure 1. BTB, CV, and NR are well-known pH indicators. The pH ranges of BTB, CV, and NR are reported to be 6.0-7.6 (from yellow to blue), 0.6-1.8 (from yellow to blue), and 6.8-8.0 (from red to amber), respectively (Hata et al., 2009). BB is an approved food colorant and widely used in ice cream, packet soups, sweets, and drinks. We are interested in BB because Hata et al. reported that polyallylamine/fluoromica composite containing BB exhibited color change induced by protonation/deprotonation of the primary amine polymer and that aqueous solutions of BB showed color change from blue to yellow through green as the pH was decreased from 10.7 to 0.0 by adding hydrochloric acid (Zumdahl, 2009). Therefore, we examined these four organic dyes to be dispersed in PSS matrix.

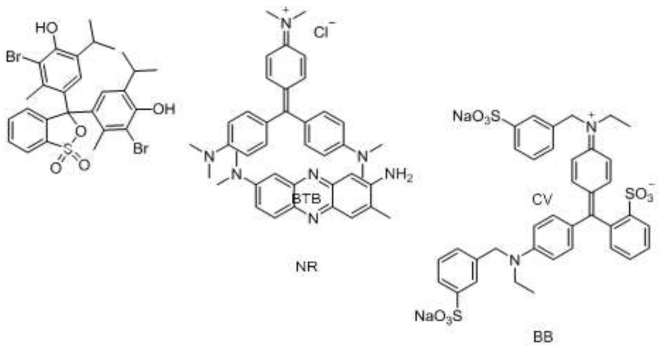

Figure 1: Chemical structures of BTB, CV, NR, and BB

Figure 2 shows color changes of humidity indicating agents composed of PSS with various organic dyes. While PSS/BTB system exhibited only a small color change on humidity, clear color changes were observed in PSS/CV, PSS/NR, and PSS/BB systems. It is noteworthy that PSS/NR composite exhibited color change from blue (low humidity) to pink (high humidity). This color change is quite similar to that of conventional cobalt-based humidity indicator. Both PSS/CV and PSS/BB composites exhibited color change from yellow (low humidity) to green (high humidity).

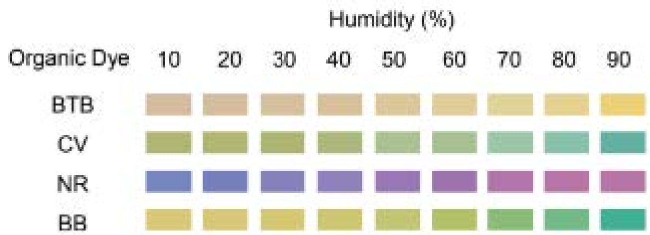

Figure 2: Color of PSS/organic dye composite from 10% (left) to 90% (right) RH

In practical use of HIC, the humidity is judged with naked eye from the color change of the indicator. Therefore, we evaluated the color change by analyzing CIE L*a*b* coordinates. CIE L*a*b* is the most complete color model used conventionally to describe all the colors visible to the human eye. It was developed for this specific purpose by the International Commission on Illumination (Commission Internationale d'Eclairage). The three parameters (L*, a*, and b*) in the model represent the lightness of the color (L* = 0 yields black and L* = 100 indicates white), its position between magenta and green (a*, negative values indicate green while positive values indicate magenta) and its position between yellow and blue (b*, negative values indicate blue and positive values indicate yellow). The relative perceptual differences between any two colors in L*a*b* can be approximated by treating each color as a point in a three-dimensional space and taking the Euclidean distance between them. The total difference, Delta E (ΔE*), is defined by the following equation.

$$\Delta E^* = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2}$$

The results of L*a*b* values for various PSS/organic dye composites were shown in Figure 3. ΔE of approximately 2.3 corresponds to a JND (just noticeable difference). The largest ΔE (12.7) was obtained for PSS/BTB composite at 80-90% RH difference. However, HICs are usually used to determine when products have been exposed to moisture above recommended storage levels that are less than 50% RH. In this regard, PSS/BB composite was the most suitable for HIC which exhibited clear color change on humidity with our naked eye among the four systems.

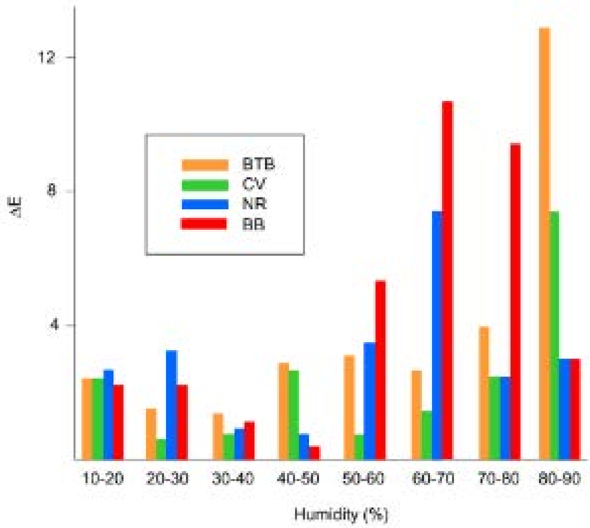

Figure 3: ΔE of PSS/organic dye composite at a 10% difference in RH

Since hydration plays an important role in color change for PSS/organic dye composite, ternary composite of PSS, organic dye, and magnesium chloride ($MgCl_2$) was examined to control degree of hydration of PSS/organic dye film. Hygroscopic $MgCl_2$ is known to be a representative deliquescent compound. Five different experiments with $[MgCl_2]/[SO_3H]$ ratio of 0.5:3, 0.38:3, 0.25:3, 0.13:3, and 0 were carried out. Figure 4 shows color changes of PSS/organic dye/$MgCl_2$ composite with various amount of $MgCl_2$. It is obvious that addition of $MgCl_2$ resulted in color toward higher humidity regions. This is probably due to the increased supply of water through hygroscopic $MgCl_2$. In the cases of PSS/BTB/$MgCl_2$, PSS/CV/$MgCl_2$, and PSS/NR/$MgCl_2$ systems, addition of $MgCl_2$ did not result in a clear color change depending on humid. On the other hand, distinct color change still remained in the PSS/BB/$MgCl_2$ composite.

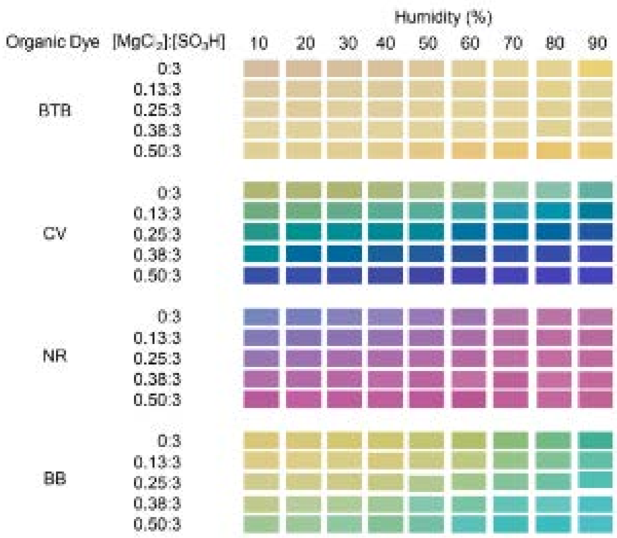

Figure 4: Color of PSS/organic dye/$MgCl_2$ composite from 10% (left) to 90% (right) RH

Ichikawa et al. explained the color change in the binary films composed of azobenzene-based molecules with p-toluene sulfonic acid in terms of reversible protonation/deprotonation. Color change observed in this work can be also explained by considering protonation/deprotonation of the organic dye dispersed in PSS matrix as shown in the Figure 5. At low humidity, the organic dye dispersed in PSS matrix should exist as a protonated form due to a large amount of sulfonic acid groups present in the polymer (equation 1). When moisture was absorbed in the composite, deprotonation will take place to convert the dye to the neutral form according to forward reaction (equation 2). That is, moisture causes color change from the color of lower pH to that of higher pH. The degree of shift of color change was dependent on the salt as a water absorbent and its wt% content. The amount of the absorbed water by the added hygroscopic compound played an important role in tuning the humidity level to be detected.

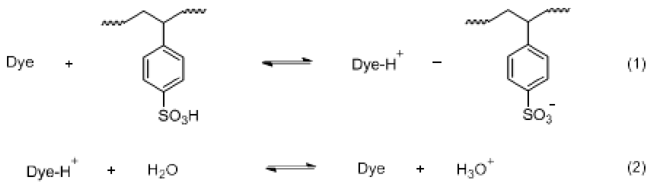

Figure 5: Plausible mechanism of color change on humidity for PSS/organic dye composite

4. CONCLUSIONS

We have demonstrated that composite of an organic dye with water-soluble acid polymer such as polystyrene sulfonic acid is considered to be a potent candidate for cobalt-free humidity indicating agent. The color of the composite film was found to change according to the environmental humidity. Evaluation of color change was done by using L*a*b* color space. Its simple preparation and ease of fabrication are the characteristic features of a good humidity indicator. Further, a ternary composite based on polystyrene sulfonic acid, organic dye and hygroscopic inorganic salt is a promising candidate for HIC because a desired humidity level can be achieved by controlling the composition. Since a wide variety of organic dyes are available, it is easy to tune color by simply changing the combination of organic dye and hygroscopic inorganic salt. Another interesting feature of our PSS/organic dye composite is its easy processability. The PSS/organic dye composite can be coated on plastic film because PSS behaves as a binder, while $CoCl_2$ can be coated only onpaper.

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