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DEVELOPMENT OF pH SENSOR SHEET FOR ACIDIC MIST OR RAIN

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It is well known that acid mist or rain have caused damages upon the living systems such as forest exposed to acidic mist, and numerous industrial products of exterior use such as concrete structures through de-alkalization followed by corrosion of rebars in concrete. The particle sizes of acidic mist or rain distributing between 10 to 100 μm in diameter, are practically meaningful to analyze the damages, and operating mechanisms. Some literatures indicate that the particle sizes were once studied using polyvinylalcohol (PVA) coated on the substrate, but pH measurement was made only with collected bulk rain [1]. Therefore, pH distribution of particle sizes was not assessed.

In our recent study, we have developed a method for measuring pH value of each mist or rain particle covering wide range of their sizes. In this study, pH values of each acidic mist or rain particles have been assessed using PVA combined with selected pH indicators.

Various PVA solutions and pH indicators were employed as starting materials for PVA/pH indicator in the form of composite films. PVA and pH indicator solutions were mixed at several ratios in the range from 1 to 10 wt% of PVA solution, and then dried at various temperature from 100 to 150 °C in order to prepare PVA/X composite film where X represents either Thymol blue (TB), Bromophenol blue (BPB), or Bromocresol green (BCG). The obtained films were sprayed with mist containing HNO_3, which was generated by a mist generator. The range of mist sizes containing HNO_3 were identified between 10 to 100 μm in diameter.

First of all, the captured mist condition on the pure-PVA film was examined. It is found that those results depend strongly on the saponification degree of PVA in spite of the viscosity and pH value of the used PVA solutions as shown in Table 1. When the saponification degree of PVA is high (No.1 ~ 4), close to its full value, the adsorbed mist did not penetrate inside the film indicating that the insufficient capture of mist particles due to the formation of (1) highly crystalline state, and of (2) numerous hydrophobic groups.

On the other hand, when the saponification degree of PVA is low (No.7), namely partial saponification due to the (1) poor crystalline state and (2) a fewer hydrophobic group, the adsorbed mist on the film surfaces penetrated rather easily into the film, and then diffused horizontally resulting in the exaggerated size and deformed shape of the mist. As a result, PVA with saponification degree of the order of 86 is found to meet the objective of this study.

Therefore, following experiments were carried out with No. 5 and 6 PVA content in order to assess the most suited combination of PVA with pH indicator, composite ratio and the drying temperature. When the films were sprayed with HNO_3 mist of pH 3, it is found that the mist mark was clearly obtained regardless of the PVA content and drying temperatures as seen in Fig. 1a) ~ c). However, the color of the marks was different from that of expected for pH 3 although all of the films were expected to show yellow for this pH 3 as in Table 2. By analyzing the preparation processes, we found that PVA/TB film exhibited slightly green after just drying without contact to acidic mist. This phenomenon suggests that pH value of PVA/TB film itself apparently shifted toward alkaline direction with increase in PVA content, and caused the neutralization of adsorbed acidic mist due to the employed PVA containing NaOH.

In order to confirm the above reasoning, the mist with pH 2 was sprayed upon the composite films to identify the critical content of PVA below which the acidic mist is confirmed by the change in right color according to the specification as shown in Fig. 1d) ~ f). The obtained results strongly suggest that the critical content of PVA is approximately 1 wt% below which the candidate films exhibit expected color change.

From the obtained results in this study, the developed composite films are practically usable for the measurement of both pH and size distribution of acidic mist or rain in the field. The combination of other pH indicators and the obtained results for the field acidic mist or rain will be presented at the meeting.

Table 1. PVA properties and the mist captured condition.

No.	Saponification / mol%	Viscosity / mPas	pH (4%soln)	Cond.
1	98.7	28.7	5.7	×
2	87.9	42.7	5.8	×
3	87.4	22.4	5.3	×
4	87.3	5.2	5.9	×
5	86.6	6.4	5.3	○
6	78 ~ 82	-	-	○
7	79.3	34.9	5.6	×

Table 2. pH indicators and those color change range.

pH indicator (X)	pH range and color
TB	1.2 (red) ~ 2.8 (yellow), 8.0 (yellow) ~ 9.6(blue)
BPB	3.0 (yellow) ~ 4.6(blue purple)
BCG	3.8 (yellow) ~ 5.4(blue)

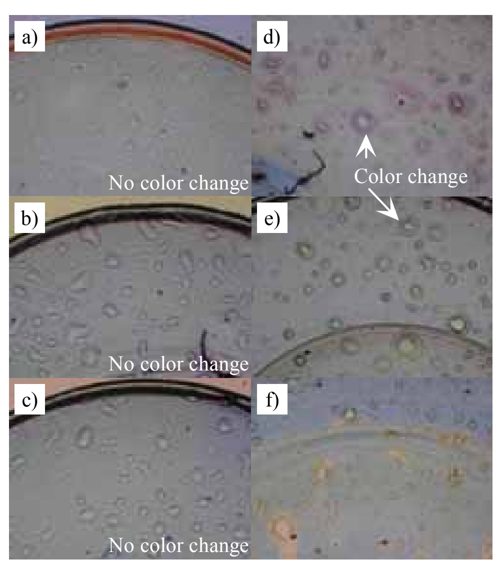

Fig. 1. The surface image of 1 wt% PVA composite films after HNO_3 mist sprayed with pH 3 (left side) and 2 (right side). PVA/TB (a, d), PVA/BPB (b, e), PVA/BCG (c, f).

Reference

1. S. J. Adams, S. G. Bradley, C. D. Stow, S. J. de Mora, *Nature*, **321**, 6073, pp. 842-844 (1986).