

Development of a Quantitative Analysis Method for Unreacted Boric Acid in Polarizing Plates

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In June 2010, the European Chemicals Agency (ECHA) added boric acid to the candidate list of SVHCs (substances of very high concern) under the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) Regulation. In polarizing plates, only unreacted (free) boric acid which is not bound to PVA is considered to be an SVHC.

We developed a quantitative analytical method for unreacted (free) boric acid remaining in polarizing plates. Unreacted boric acid can be extracted selectively from polarizing plates with 2-ethyl-1,3-hexanediol / chloroform, and analyzed by ICP-AES.

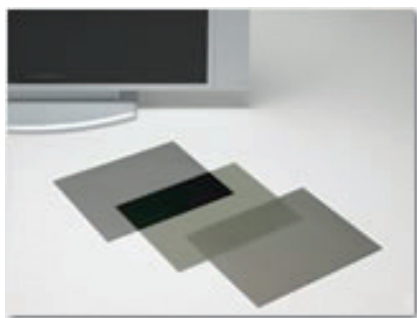
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Introduction

1. What Are Polarizing Plates?

Polarizing plates are indispensable materials for liquid crystal displays (LCDs), and are one of the major products of the IT-Related Chemicals Sector of Sumitomo Chemical (Fig. 1).¹⁾ The function of polarizing plates comes from polarizers, which are polymer films having polarizing properties. Iodine-dyed polyvinyl alcohol (PVA) films are well known as polarizers (Fig. 2).

Polarizing is the property of absorbing light along the orientation axis of a film (dichroism), which comes from uniaxially oriented elongate-shaped pigments in the uniaxially stretched polymer film (Fig. 3, 4).



Polarizing plates

Fig. 1 LCD panel and polarizing plates

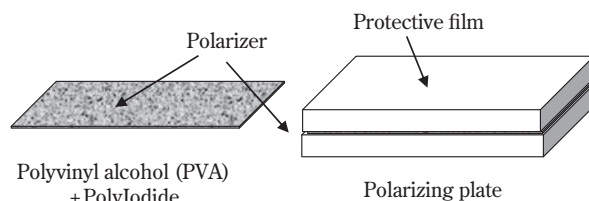


Fig. 2 Polarizer and polarizing plates

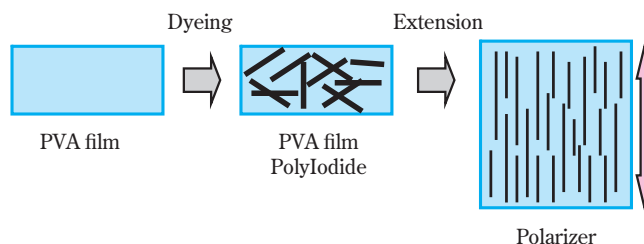


Fig. 3 Production method of polarizer

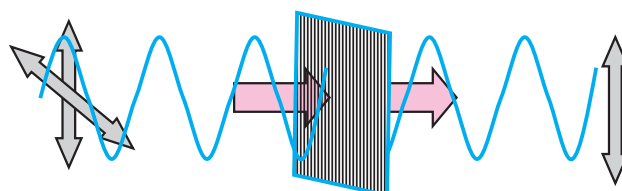


Fig. 4 Dichroism of polarizer

The role of a shutter that can turn light transmission on and off using an electrical signal can be achieved by incorporating a polarizing plate that has this optical filtering function known as dichroism. Fig. 5 is a schematic diagram of a twisted nematic (TN) type liquid crystal panel. By attaching two polarizing plates, one to each of the upper and lower surfaces of a liquid crystal display panel so that the absorption axes are orthogonal, light is not transmitted in a state (electric signal ON) where the liquid crystals are lined up perpendicular to the screen. In the state (electric signal OFF) where the liquid crystals are twisted 90° to be parallel to the screen, light is transmitted. Here, the ellipses schematically show the rod-shaped liquid crystal molecules, and the longitudinal direction corresponds to the longitudinal direction of the liquid crystal molecules. The electric signal for the liquid crystal for the green color filter is in an OFF state, and by arranging the liquid crystal molecules so they are twisted 90°, the light passing through the liquid crystal layer is also rotated (optical rotation) 90°; therefore an element where the light can pass through the liquid crystal panel is shown.

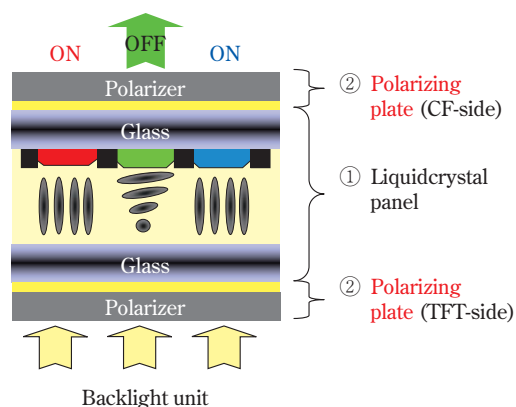
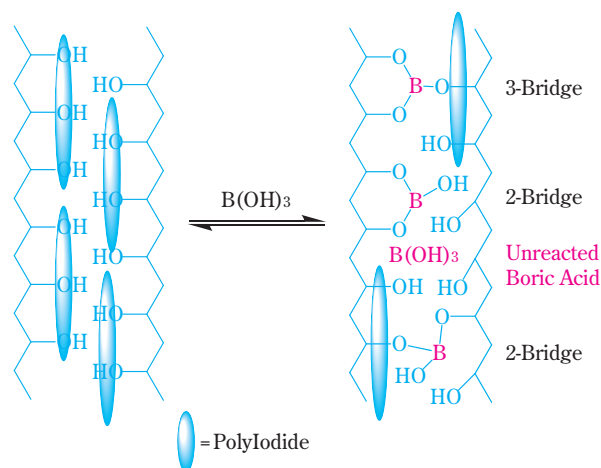


Fig. 5 LCD panel (TN mode)

In the widely-used iodine-type PVA polarizing plates, iodine-dyed PVA films, which are drawn and cross-linked in a hot boric acid solution to improve their durability by creating a cross-linked internal structure (Scheme 1) are used as polarizers. In addition, to increase the mechanical strength of the thin film polarizer, protective films are applied to both sides. In other words, a polarizing plate is formed from a laminated structure, in which a PVA film containing iodine and boric acid is bonded between the two protective films (Fig. 2).



Scheme 1 Reaction of polarizer with boric acid

2. Restrictions on Chemical Substances Possibly Related to Polarizing Plates — Boric Acid

In June 2010, the European Chemicals Agency (ECHA) designated boric acid (CAS No. 10043-35-3, 11113-50-1) as a candidate substance for substances of very high concern (SVHC) in the EU registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation. According to the regulation, suppliers may have some legal obligations in accordance with the content of SVHC in their product. In the case of polarizing plates, if the boric acid content exceeds 0.1 % (w/w), suppliers must provide sufficient information to their customers, and, in addition, if the total amount of boric acid in polarizing plates for the EU is above 1 ton per year, supplier have an obligation to notify the ECHA.

The important point is that the target of “boric acid” in the SVHC restriction is unreacted boric acid, that is, $B(OH)_3$, and not the boric acid bonded to hydroxyl groups in the PVA (Sumitomo Chemical’s opinion). For this reason, we need an analytical method which can distinguish between these two types of boric acid, and quantify only the unreacted boric acid accurately.

As described above, the cross-linking treatment with boric acid is applied to iodine-type PVA polarizing plates, but it can be assumed that in the manufacturing process, almost all of the unreacted boric acid can be eliminated by washing after the cross-linking treatment. However, as we will discuss later, if we attempt to analyze the unreacted boric acid in polarizing plates, the amount of boric acid increases due to the hydrolysis of the cross-linked parts, or the unreacted boric acid reacts with PVA in the preliminary heating processes for analysis. Due to these problems, there has been no effective method for

analysis, so we could not accurately quantify the amount of unreacted boric acid in polarizing plates.

[Notes]

ECHA : European Chemicals Agency

REACH: European Registration, Evaluation, Authorization and Restriction of Chemicals system

3. Purpose and Overview of Results

Boric acid has become a target of REACH regulations, but in a situation where there is no useful method for accurate assay of the unreacted boric acid in polarizing plates, there has been a risk of spreading analytical results which are different from the actual content results due to measurements after inappropriate preliminary treatments. So, to comply with the Regulations, it became an urgent matter to develop an accurate content analysis method for the unreacted boric acid in polarizing plates. To fulfill this requirement, we developed a quantitative analytical method for unreacted boric acid in polarizing plates.

Specifically, a method of freezing and pulverizing polarizing plates into microparticles, and chelating extraction with a chemical compound that chelates only unreacted boric acid, made it possible for us to extract unreacted boric acid separately from polarizing plates

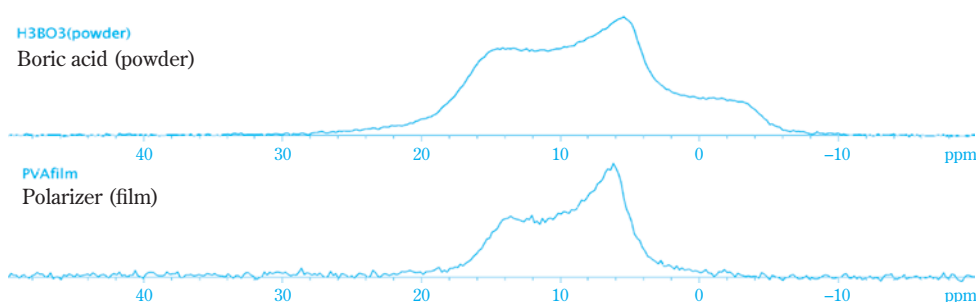
in a solid state and to determine their quantities. In the following, a detailed report will be given on this research.

Analytical Study

Many methods, such as (1) atomic absorption, (2) chromogenic method and (3) ^{11}B -NMR are known for quantitative determination of boron.^{2),3)} To select methods that match the purpose described above, the most important points were absolutely no observation of the boric acid which was cross-linked with the PVA, and being able to quantitatively determine only the unreacted boric acid.

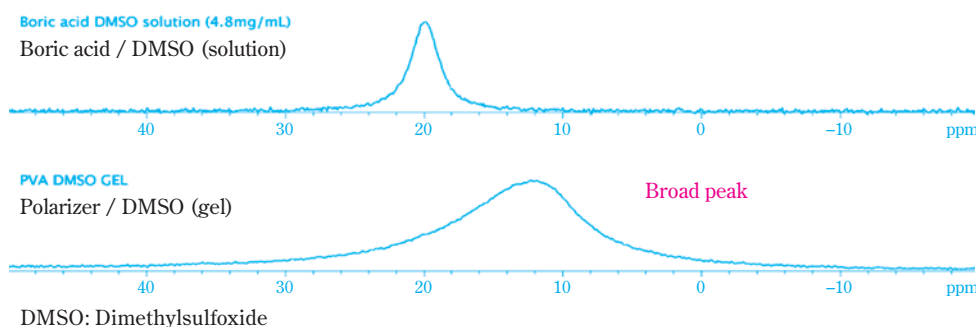
1. Solid-state ^{11}B -NMR Measurements

We have investigated whether solid-state NMR could distinguish unreacted boric acid from bridged boron. Fig. 6 shows the solid-state ^{11}B -NMR spectrum of boric acid and the polarizer. While there is a difference between the two, there is a broad signal in the same shift position; therefore, it was determined that differentiation and quantitative determination would be difficult. But HR-MAS only gave a broad signal, and definitive assignment and quantification of boric acid were difficult (Fig. 7).



Varian NMR System PS400WB
 • 9.4T(400MHz)
 • 4mm ϕ Solid State
 • 11B(OBNUC)
 • MAS (kHz) 0, 5, 16*
 • Single Pulse
 • 2 to 2048 SCANS
 * Solution: 0kHz, Gel: 5kHz,
 Film or Solid: 16kHz

Fig. 6 Solid state ^{11}B -NMR spectrum of boric acid and polarizer



Varian NMR System PS400WB
 • 9.4T (400MHz)
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 • MAS (kHz) 0, 5, 16*
 • Single Pulse
 • 2~2048 (POINT)
 * Solution: 0kHz, Gel: 5kHz,
 Film or Solid: 16kHz

Fig. 7 ^{11}B -NMR spectrum of boric acid (solution) and polarizer (gel)

On the other hand, structural analysis of iodine-based polarizing plates using solid-state NMR is commonly carried out, and research is being done on the effects on boron bridging state analysis, PVA orientation, optical performance and heat resistance.⁴⁾ Remarkable progress is being made in increasing the sensitivity and increasing the resolution of solid-state NMR; therefore, there are expectations in the future for analyzing unreacted boric acid in a solid state using solid-state NMR analysis.^{5), 6)}

2. Solution ^{11}B -NMR Measurements

Solvents for extracting and carrying out quantitative determination on only the unreacted boric acid from polarizers (PVA + boron bridging) were investigated. Quantitative determinations of boric acid using NMR measurements were investigated so as to be able to confirm PVA dissolution behavior.

Cut pieces (approximately 10 mg) of a PVA polarizer approximately 1 cm square were put into a screw-cap tube and immersed in 0.7 mL of various deuterated solvents. After two days at rest, NMR measurements were carried out on the solution part (Table 1). In deuterium oxide, boron could be detected regardless of the temperature. On the other hand, PVA which is the base material was not detected at 5°C, and a minute amount was detected under room temperature conditions. Because breaking of boron bridging and dissolution of PVA can be considered, the changes over time were checked, and the dissolution of PVA was slow (Fig. 9) and the elution of boric acid at room temperature was rapid (Fig. 8).

Table 1 Solvent and solubility

Solvent	Temp.	^1H -NMR (PVA)	^{11}B -NMR (Boric acid)	PVA in Solvent (Polarizer)
D_2O	rt	Detected	Detected	Swelling
D_2O	5°C	Not detected	Detected	No change
CDCl_3				
DMSO-d_6 ,	rt	Not detected	Not detected	No change
Acetone- d_6 ,				
Methanol- d_4				

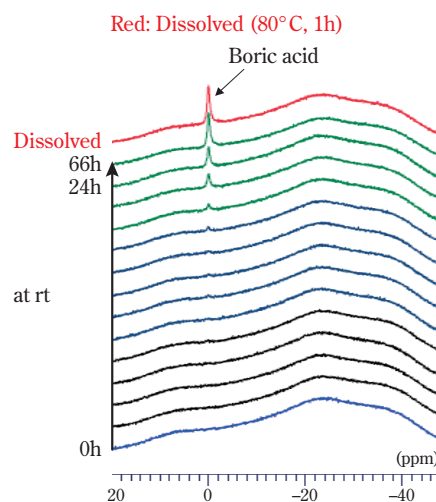
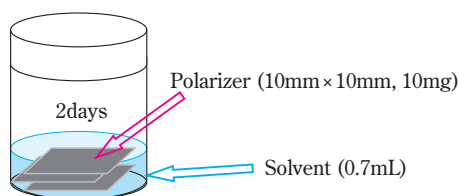


Fig. 8 ^{11}B -NMR spectrum of boric acid (D_2O solution)

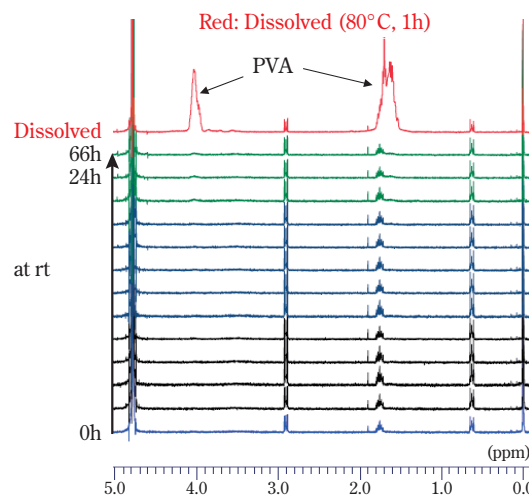


Fig. 9 ^1H -NMR spectrum of polarizer (D_2O)

From the results above, there was no remarkable dissolution of PVA, but breakdown of bridging occurred when water was used as the extraction solvent, and it was possible to confirm elution of boric acid from the polarizer (Fig. 10). Therefore, it was determined that

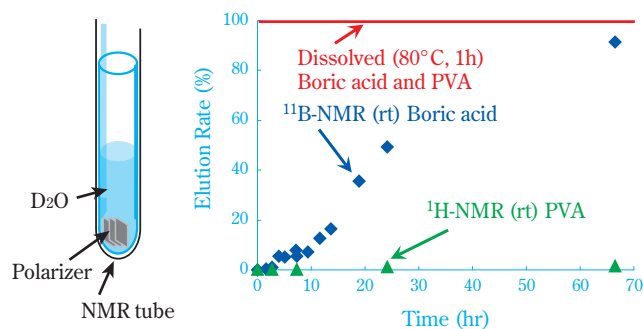


Fig. 10 Correlation of an elution rate and time

for the extraction of the unreacted boric acid, a solvent that does not break the PVA-boric acid bridging should be used.

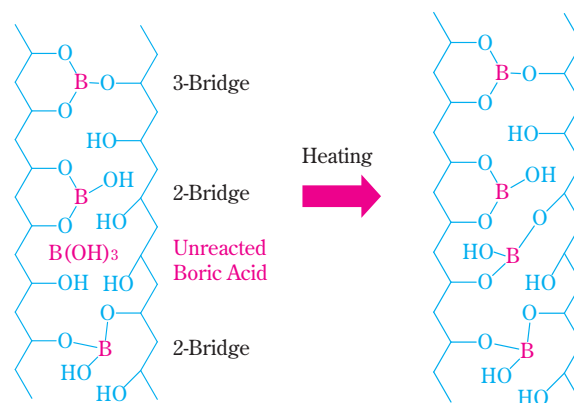
3. Investigation of Chelate Extraction Method

Extracting boric acid in an organic solvent layer directly and efficiently by separation or another operation is difficult; therefore, derivatization methods that chemically convert the boric acid into a derivative which is easily extracted in organic solvents such as boric-acid ester are well known as methods for boric acid analysis.⁷⁾ However, a heating pretreatment is typically carried out in derivatization methods. If a polarizing plate is the object of the analysis, a cross-linking reaction with the unreacted boric acid like that in **Scheme 2** would be anticipated in the heating pretreatment.

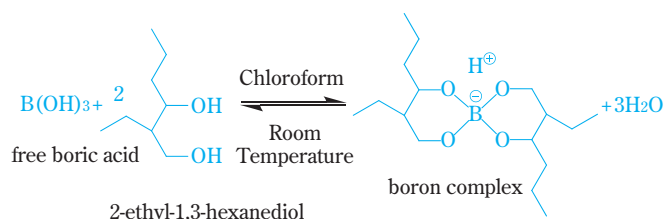
On the other hand, there are also various investigations into other boric assay methods⁸⁾ that carry out chelate extraction in mild conditions such as room temperature without heating, but the ones that are publicly known are assay methods for boric acid in water. There has not been any method for efficiently extracting unreacted boric acid in a solid state in an organic solvent. Application of this chelate extraction method to a non-aqueous system was tested as follows.

(1) Investigation of non-aqueous extraction method

An extraction method that use dihydric alcohol 2-ethyl-1,3-hexanediol which makes a complex with boron and makes it soluble in chloroform, was investigated (**Scheme 3, Table 2**).²⁾



Scheme 2 The reaction of PVA with boric acid



Scheme 3 The reaction of boric acid with 2-ethyl-1,3-hexanediol

Table 2 Solubility of boric acid

Sample	Solvent	Temp.	¹ H-NMR (PVA)	¹¹ B-NMR (Boric acid)
Boric acid (powder)	CDCl ₃	rt	Not detected	Not detected
Boric acid (powder)	CDCl ₃ + 2-ethyl-1,3-hexanediol	rt	Not detected	Detected

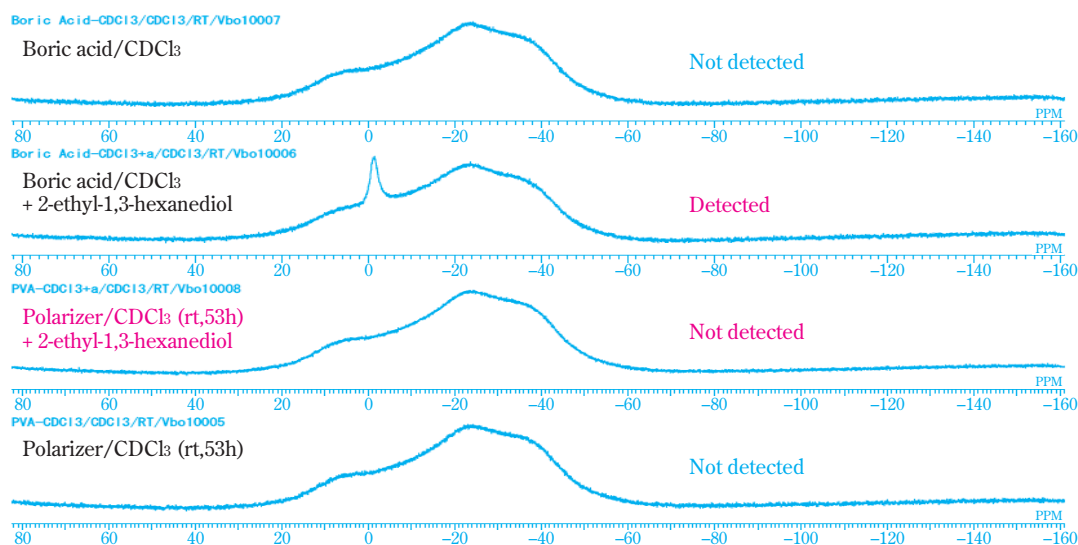


Fig. 11 ¹¹B-NMR spectrum of extraction solution

From the results of ^{11}B -NMR, the possibility of extracting a chelated complex in which boron and the dihydric alcohol form a boron complex in a chloroform solution without dissolving the PVA or boric acid could be confirmed. On the other hand, the sensitivity of the boron detection with NMR was insufficient, and the necessity for investigating methods for efficient extraction from solid-state polarizing plates was foreseen (Fig. 11).

(2) Freezing and pulverizing method

Generally, extraction of internal target components without dissolving solid-state samples in a molded product state is difficult. Methods for extracting by pulverizing a sample into microparticles and increasing the surface area are typical, but in the case of polarizing plates, the alteration in samples should be taken account of because of the progression of the cross-linking reaction due to heat and reactions breaking down the bridging due to absorption of moisture.

Therefore to eliminate the effects of heat, we decided to make samples into microparticles by freezing and pulverizing. In terms of the size of the microparticles, consideration was given to the polymer flow scheme pretreatment method in the Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, which is known as a method for evaluating soluble components in polymers. It was assumed that an efficiently small particle size that would be sufficiently high for the extraction was obtained by forming a fine powder from the polarizing plate by the procedure below (Fig. 12).

An example of the particle size distribution when a polarizer was actually frozen and pulverized is shown in Fig. 13. A pulverized material whose size is smaller than No. 60–80 mesh particle size (400–300 μm), which is the goal of the polymer flow scheme, was

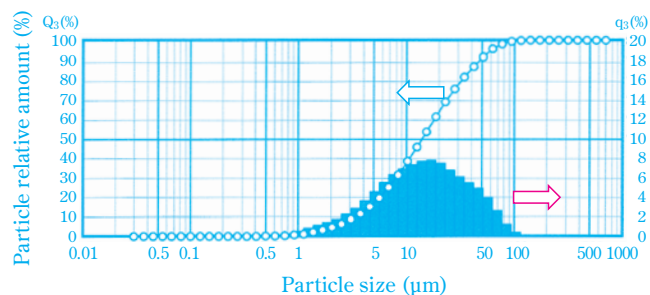


Fig. 13 Particle size of fine powder derived from a polarizer

obtained. So it could be assumed not to have any problems as a sample for chelating extraction of unreacted boric acid.

[Procedure]

- Cutting** : a polarizing plate was cut into 2–5 mm squares under an inert gas atmosphere and put into a pulverizing container.
- Freezing** : freezing was carried out by cooling for seven minutes in liquid nitrogen.
- Pulverization**: pulverization was carried out in a freeze crusher for about 5–10 minutes.
- Removal** : the powdered sample was collected after returning to room temperature without changing the inert gas atmosphere.

(3) Analysis of polarizing plate

The method of extraction using 2-ethyl-1,3-hexanediol can selectively extract the unreacted boric acid targeted for analysis in a chloroform layer; therefore, if quantitative determination of boron is carried out, quantitative determination of the unreacted boric acid is possible with a boric acid conversion.

Even if the unreacted boric acid in the polarizing plate is a minute amount, a highly sensitive assay is possible with inductively coupled plasma measurements;

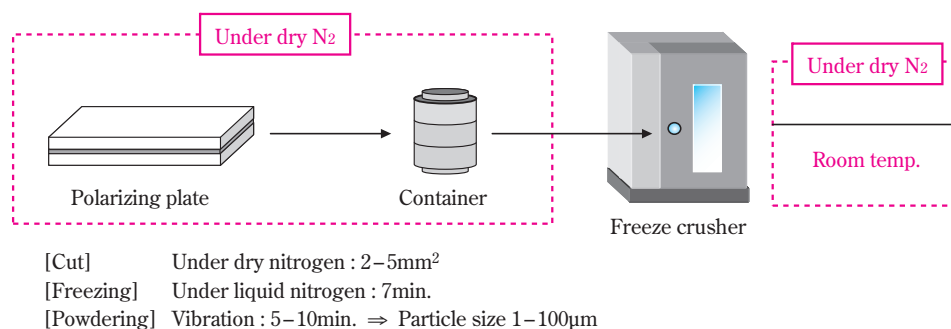


Fig. 12 Preparation method of fine powder

therefore, they were selected as the method for analyzing the boron content (calibration curve: boron reference solution, lower limit for determination: 1 µg/g (1 ppm)).

(i) Confirmation of effects of freezing and pulverizing

There is a concern that microparticles formed by freezing and pulverization absorb moisture. Therefore, to check the effects of moisture absorption during pulverization and pretreatment for the assay, freezing and pulverization in an air atmosphere and exposure of the microparticles to air were carried out, and the values for boron content were compared. Here, the experiments were carried out with a polarizer that was thought to be more easily affected by the atmosphere than a polarizing plate.

As shown in **Table 3**, even if a sample is put into the pulverizing container and pulverized in an air atmosphere, and even if the sample that has been made into microparticles is kept in an air atmosphere, the analytical values did not change even though the boron content tended to increase slightly. There was no sudden increase in the boron elution due to the moisture absorbing properties of the frozen and pulverized sample and the breakdown of bridging. Changes in the weight of the frozen and pulverized samples due to the air atmosphere were confirmed, and there was a

roughly 1% increase in weight (presumed to be moisture absorption) in several hours. They were stable thereafter, and no trend toward absorption of moisture over time could be seen.

From the results above, the effects of humidity on samples formed into microparticles by freezing and pulverization were smaller than predicted, and the effects of moisture absorption into the pulverized samples on the analysis of unreacted boric acid was thought to be negligible.

(ii) Boric acid addition tests

The validity of chloroform extraction-inductively coupled plasma analysis was verified using a model sample in which boric acid was added to commercial PVA powder that did not include boric acid. Boric acid in a weight equivalent to 0.2%–2% of the PVA was added, and in the results of the quantitative analysis, an excellent recovery rate was obtained even though the numbers were somewhat high (**Table 4**). The reason that the recovery rate increased at a constant rate was assumed to be because the chloroform in the solution decreased because the PVA powder absorbed chloroform and the apparent boric acid concentration increased. Compared with polarizers and polarizing plates, it has been confirmed that commercial PVA powder absorbs a greater amount of chloroform and it becomes swollen in the solution.

Table 3 Amount of unreacted boric acid in polarizer

	Freeze Powdering (Condition)	Extract condition	B content (ICP-AES) (µg/g)	B content (wt%)	Measured [B(OH) ₃] (%)
1	Freeze Powdering (Under Air)	Under Air 24 h, at rt	8	0.04	0.2
2	Freeze Powdering (Under Dry N ₂)	Under Dry N ₂ 24 h, at rt	7	0.03	0.2
3	Freeze Powdering (Under Dry N ₂)	Under Air 24 h, at rt	8	0.04	0.2

ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectrometry
Extract solution: 2-ethyl-1,3-hexanediol/chloroform (10/90 v/v)

Table 4 Amount of boric acid in PVA powder

	Amount of Boric acid addition	Weighing Value (mg)	B Content (ICP-AES) (µg/g)	B Content (wt%)	Boric Acid (wt%)	Addition Recovery Rate (%)
1	0.2%	PVA: 514.0 Boric acid: 1.1	54	0.052	0.29	140
2	1.0%	PVA: 515.3 Boric acid: 5.0	240	0.231	1.30	130
3	2.0%	PVA: 506.5 Boric acid: 10.0	500	0.489	2.75	140

(iii) Analytical results for polarizing plate

Quantitative analysis of unreacted boric acid was carried out with actual polarizers and polarizing plates (Table 5). Polarizer 1 in measurement example 1 was a polarizer for which the washing after the cross-linking process during production was more intensified than that for Polarizer 2 in measurement example 2, and the difference in the amount of unreacted boric acid could be analyzed. Furthermore, in measurement example 3 for a polarizing plate created with Polarizer 2, the amounts of unreacted boric acid were valid in calculations from the composition ratio of the polarizer and protective films.

From the results above, it can be assumed that accurate quantitative analysis of unreacted boric acid remaining in polarizing plates can be carried out by this method using 2-ethyl-1,3-hexanediol/chloroform solution as a chelating agent.

(iv) Reconfirmation of validity of sample pretreatment.

Using the same Polarizer 1 as in Table 5, a comparison of the effects (comparison of 2-ethyl-1,3-hexanediol/chloroform solution and water) of freezing and pulverization and solution extraction was carried out (Table 6).

Even if immersed in an extraction solution for one week, the unreacted boric acid in a sample that had not been formed into microparticles by freezing and pulverization could not be extracted in the chloroform

layer. In addition, with extraction by water, it was confirmed that the bridging was gradually broken down at room temperature and boric acid was eluted in the water layer.

From the results above, it was determined that a combination of forming microparticles by freezing and pulverization and nonaqueous extraction by the 2-ethyl-1,3-hexanediol/chloroform solution is essential for quantitative analysis of the unreacted boric acid in polarizing plates.

Summary

The results of our investigation this time into an assay method for unreacted boric acid in polarizing plates are summarized in the following. This assay method is one that can selectively extract the unreacted boric acid from polarizing plates, which are easily affected by water and heating, under simple, mild conditions, and it is a method for quantitative determination that will be useful for making determinations in response to REACH regulations. In addition, this assay method is one that is not limited to polarizing plates and can be applied widely to polymer compounds.⁹⁾

- (i) Polarizing plates (and polarizers) react with water, and the cross-linked parts can easily be eluted; therefore, a nonaqueous assay method was necessary.

Table 5 Amount of unreacted boric acid in polarizer

	Measurement 1	Measurement 2	Measurement 3
Sample*	Polarizer 1	Polarizer 2	Polarizing plate
Pre-cut	1cm square	2–5mm square	
Freeze powdering	Freeze powdered	Freeze powdered	Freeze powdered
Extract solution	2-ethyl-1,3-hexanediol / chloroform (10/90 v/v)		
Extract condition	24 h, at rt	24 h, at rt	24 h, at rt
Measured [B(OH) ₃]	0.2wt%	0.37wt%	0.054wt%

* Polarizer 1 was rinsed with water more strongly than Polarizer 2.

Polarizing plate consists of the three layer of Protective film A / Polarizer 2 / Protective film B.

Table 6 Amount of unreacted boric acid in polarizer

	Measurement 4	Measurement 5	Measurement 6
Sample	Polarizer 1	Polarizer 1	Polarizer 1
Pre-cut	2mm square		
Freeze powdering	Non Freeze powdered	Non Freeze powdered	Non Freeze powdered
Extract solution	2-ethyl-1, 3-hexanediol/chloroform (10/90 v/v)	D ₂ O	
Extract condition	168 h, at rt	168 h, at rt	1 h, at 80°C
Measured [B(OH) ₃]	< 0.01wt%	8.7wt%	22wt%

- (ii) Polarizing plates formed into microparticles were stable and insoluble in chloroform.
- (iii) The unreacted boron in polarizing plates is selectively extracted into a chloroform layer by a 2-ethyl-1,3-hexanediol/chloroform (10/90) solution, and high sensitivity quantitative determination was possible with inductively coupled plasma analysis.
- (iv) The reaction for the chelate extraction of unreacted boric acid proceeds efficiently at room temperature.

Conclusion

The recent developments in analytical equipment have been remarkable, and devices with higher sensitivity and higher resolution are being developed and announced one after another. Progress in new pretreatment techniques and measurement methods is rapid, and assays and analysis that were difficult up to now have become possible with higher speed, multi-sample analytical processing and the possibilities for “in-situ” observations in reactive conditions or carrying out non-destructive local analysis. Examination of these new techniques and investigations of their introduction not only represent a raising of the level of analytical techniques, but also have an important effect on contributions to product development and resolution of problems.

On the other hand, analytical frameworks in which typical chemical analysis and pretreatment methods as well as techniques and know-how such as equipment management frameworks have been integrated and for which techniques have been accumulated for a long time cannot be achieved overnight. It can be assumed an important role will be played in research and development by providing optimal assay methods that match the trends in research.

In this assay method for unreacted boron in polarizing plates, typical chemical analysis was used for the chelate extraction method, which was the assay method for minute amounts of boric acid in water, and for the freez-

ing and pulverizing method for improving the extraction efficiency. This is a matter where analysis with only high sensitivity analytical equipment is difficult, and we think that pretreatment that stabilizes samples for measurement and sampling are important for unstable samples and minute amounts of analytical targets that are in a state of equilibrium. Moving forward, we would like to put effort into examining and introducing the latest techniques as well as building up sample handling techniques.

[Notes]

The results of this research were presented at The 18th International Display Workshops (IDW) 2011 held in Nagoya in December 2011, and received the IDW Outstanding Poster Paper Award.

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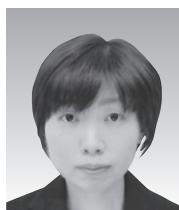
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