

Antifogging Effect of Cellulose Films by Chemical Modification of the Surface Using Nonionic Fluorocarbon Surfactant

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Synopsis

Wettability and antifogging effect on the surface of the transparent thin film of cellulose esters were studied by fixing chemically nonionic fluorocarbon surfactants on the film surface and were compared with the properties of the surface fixed with the corresponding nonionic hydrocarbon surfactants. These antifogging properties on the surfaces covered by the monomolecular layer of fluorocarbon surfactant were found to be more excellent than those of the nonionic hydrocarbon surfactants from the measurement of contact angle for water droplets and also from the data of Zisman's plots. The surface of the thin film setting in the closed chamber filled with water vapor at 60°C were confirmed to be transparent during a long time without fogging. Antifogging effect may be due to so-called double structure consisting of fluorocarbon and nonionic ethyleneoxide chains in the monomolecular layer.

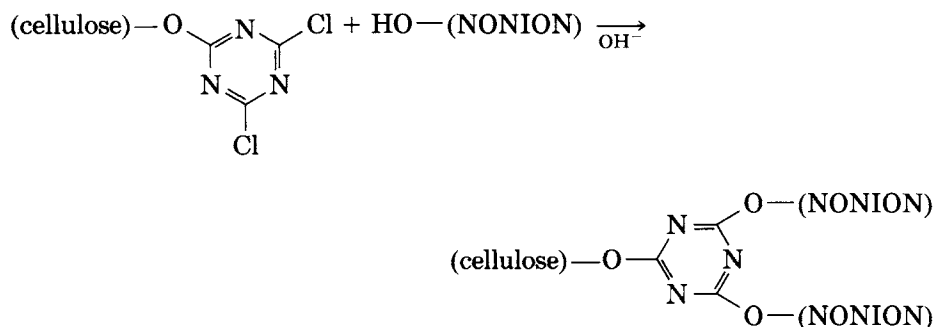
INTRODUCTION

Many workers have so far reported the improvements of the wettability of hydrophobic polymer, water repellent of the hydrophilic polymer, or the interaction between adhesive and adherent surfaces and so on.¹⁻⁶ In particular, several studies have been done related to the introduction of the polar groups by the surface oxidation with chromic acid mixture⁷ or chlorate,⁸ cold plasma,^{2,3,9,10} and surfactant spreading on surfaces of polymers.¹¹

In general, transparent polymer surfaces with hydrophobic properties are liable to deposit small droplets of water on the surfaces in water vapor and then to produce an opaque fogging. This becomes a big problem for practical applications such as windowpanes, glasses, and mirrors. The opaque fogging can be prevented by putting either water repellent or hydrophilicity on the polymer surface, the so-called antifogging effect.¹¹⁻¹³ For example, surfactants spread on the polymer surface or surfactants blended into the bulk of the polymer usually are more effective for antifogging, but these cannot be maintained for a long time. Cellulose esters themselves have some of this antifogging effect and are used in many fields. However, this effect is not enough because the surfaces are easily contaminated by oil, etc., and polar groups exposed on the surfaces migrate gradually into the bulk of the polymer.^{14,15}

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At first the plates after hydrolysis were treated with a solution of cyanuric chloride in a dioxane–water mixture (1 : 4 200 mL) in a flask cooled in ice water bath. After 5 min, the solution was adjusted at pH 5 and washed with 200 mL of dilute HCl solution of pH 5, and besides then with water. Immediately, the plates were dipped for 10 min in 200 mL of solution containing 10^{-5} mol of nonionic surfactants at 25°C to react with cyanuric acid on the surface as follows:



Then 6 mL of 1N KOH were added. After 10 min, the plates were taken off and washed with a quantity of water, and then 10 sheets of the plates were

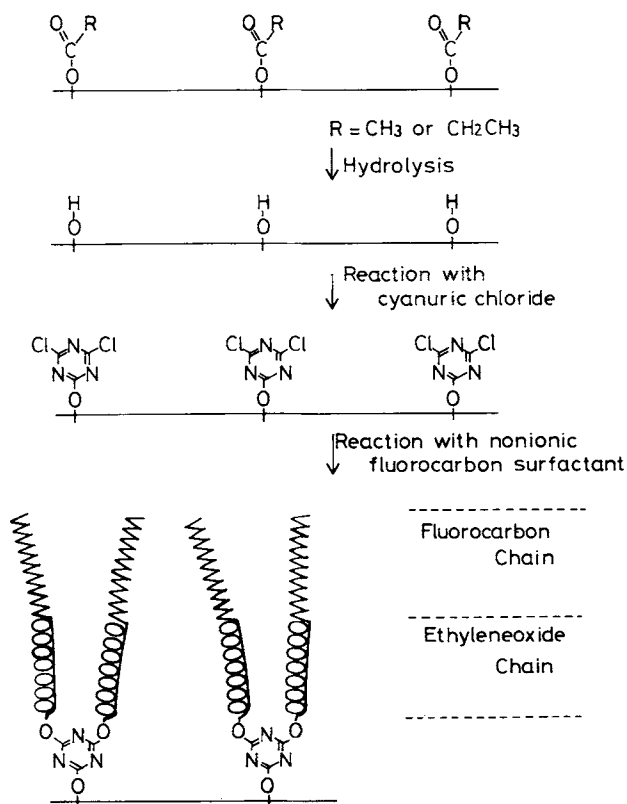


Fig. 1. Reaction scheme.

dipped all together into pure water of 50 mL for 24 h at 25°C. As the surface tension of the water used to dip the plates was measured at 25°C after 24 h, and the value was found to be consistent with one of pure water even after 24 h, it was decided to completely wash out the surfactants almost adsorbed in the plates. The plates were stored in vacuum. These procedures from the hydrolysis to the fixation of surfactants are schematically shown in Figure 1.

*The Quantitative Assay of Surfactants*²⁰

Samples. Plates reacted with surfactants were treated in a solution of 10% HCl (50 mL). After 1 h, the plates were taken out, and washed with 20 mL of water and then 30 mL of aqueous NaOH solution was added to adjust at pH 7. The solutions of 100 mL obtained here were taken as samples 1.

Reagent. A mixture containing 620 g of ammonium thiocyanate (NH_4SCN) and 280 g of cobalt nitrate hexahydrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] were dissolved in water and diluted to 1 L, and a trace of impurity in the solution was removed by extraction into the benzene phase.

Procedure. Sample 1 was put into a separating funnel, and 15 mL of ammonium cobalt thiocyanate reagent and 20–25 g of sodium chloride were added. The solution was shaken and left to stand for 15 min. The color of the solution became blue due to formation of a complex of the surfactant with the reagent. Benzene (25 mL) was accurately added to the funnel. The solution was shaken for 1 min and left to stand for 1 h to allow the layers to separate. As the complex transferred to the upper benzene layer, the lower aqueous layer was discarded. The upper benzene layer was centrifuged for 10 min. The amount of the complex in the upper layer of the benzene solution was estimated by measuring the absorbance at λ maximum of 320 nm using a UV spectrophotometer (Shimadzu UV-160).

Critical Surface Tension Measurements

Contact angles were measured using the Wilhelmy plate method.^{21,22} The equipment was closed in temperature-controlled thermostat maintained at $25 \pm 0.5^\circ\text{C}$. The plate was hung at hook of electrobalance (Shimadzu AE-163). The bottom of the plates was set horizontally. The beaker containing liquid was then raised until the bottom edge of the plate touched the liquid, and then lowered slowly until the bottom edge of plate was in the plane of the liquid. Contact angles were calculated from following equation:

$$mg + B = P\gamma \cos \theta \quad (1)$$

where m is the mass of the plate (g) as measured via electrobalance, g is the local gravitational force (979.8 dyn/g), B is buoyancy, P is the perimeter of the plate, and γ is the surface tension of the wetting liquid (mN/m). The affect of the buoyancy was small, and it could be negligible.

Glycerin–water mixtures with various ratios and aqueous solutions of nonionic surfactant, $\text{C}_{10}\text{H}_{21}\text{O}(\text{CH}_2\text{CH}_2)_8\text{H}$ (abbreviated here after as C_{10}E_8), with homogeneous ethyleneoxide chain length as listed here were used to determine the critical surface tension, γ_c , values of the plate surfaces, as we have so far confirmed that the γ_c value obtained by using nonionic surfactant

coincides with that obtained from the series of *n*-alkanes²³:

Liquids	γ_1 (mN/m)
Water	72.4
Glycerin : water	
1 : 3	70.0
1 : 2	68.5
1 : 1	66.5
2 : 1	65.5
Nonionic surfactant (C ₁₀ E ₈)	
Aqueous solutions	
(1) 2.2×10^{-5} mol/L	58.0
(2) 6.7×10^{-5} mol/L	53.0
(3) 2.2×10^{-4} mol/L	46.0
(4) 6.7×10^{-4} mol/L	39.0

These γ_c values before and after hydrolysis, and after reaction with each nonionic surfactant were determined from Zisman's plots.⁵ Surface tensions for the solutions were measured at 25°C by using a Wilhelmy-type surface tensiometer (Shimadzu ST-1).

Antifogging Effect

The antifogging effect was confirmed by comparing the extent of clouding of plates before and after hydrolysis and after reaction of each surfactant in the closed chamber filled with water vapor at 60°C.

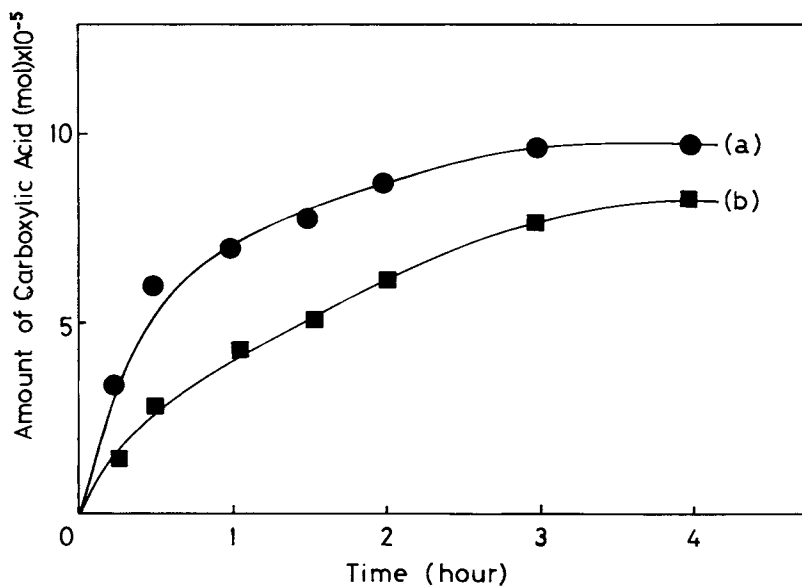


Fig. 2. Hydrolysis curve of cellulose ester: (a) cellulose acetate; (b) cellulose propionate.

RESULTS AND DISCUSSION

Hydrolysis of Polymer Surface

Figure 2(a) shows the amounts of acetic acid hydrolyzed during a certain period from surface per unit area. If only the ester on the surface was hydrolyzed, the amounts of hydroxyl groups appeared on the surface can be estimated from this curve in Figure 2(a). The amount of the hydrolyzed acetic acid reached a constant value at about 3 h. However, when the polymer surface was hydrolyzed for 1 h, the density was 6.5×10^{-5} mol/cm². This value means that surface of cellulose acetate is completely hydrolyzed compared with theoretical value 1×10^{-9} mol/cm². From this result, hydrolysis time was determined as 1 h. The hydrolysis time of cellulose propionate was similarly determined as 1 h from Figure 2(b).

The Quantitative Assay of Surfactant

The relation between removal time of surfactant from polymer surface and amount of surfactant removed from the surface is shown in Figure 3. It shows that the amount of surfactant removed from the surface becomes virtually constant at 1 h.

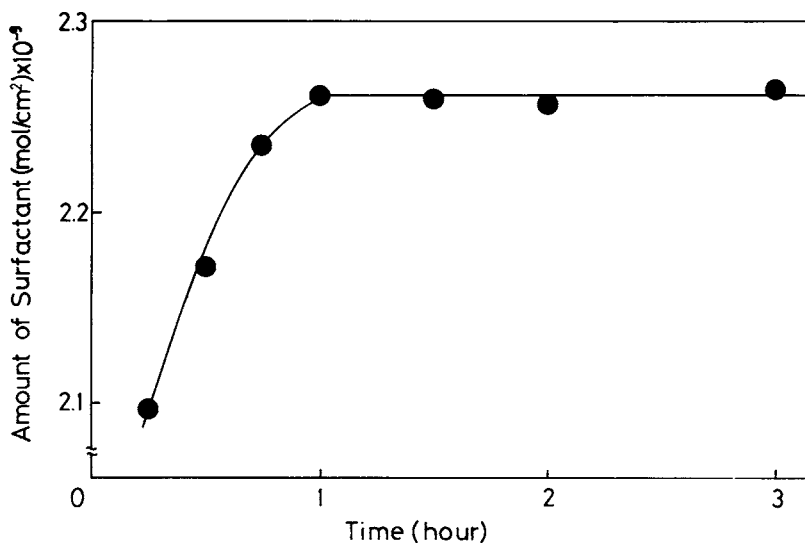
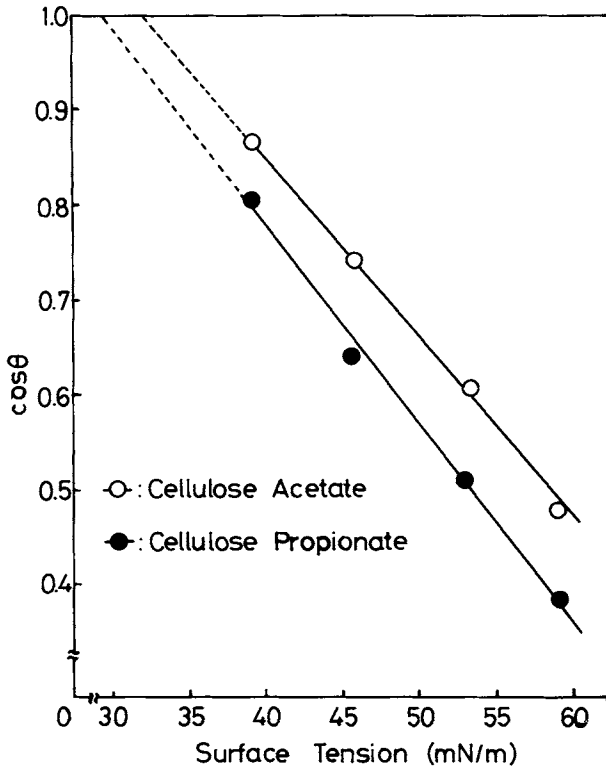


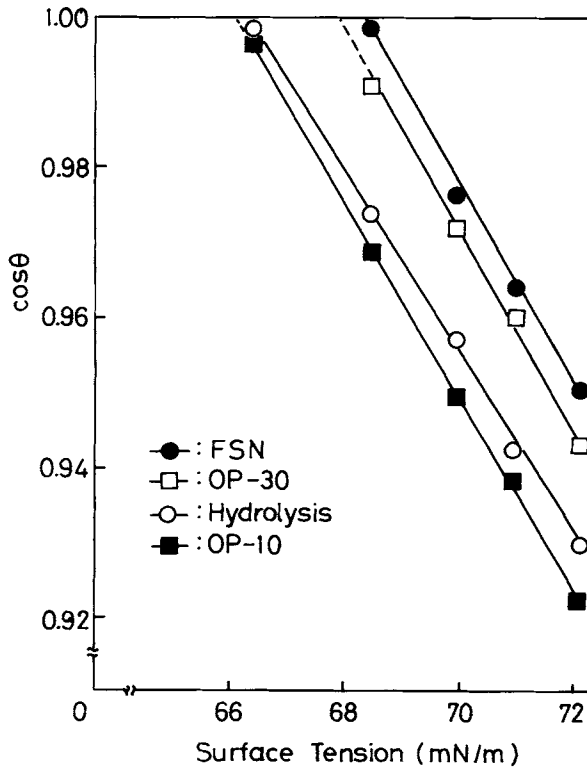
Fig. 3. Removal time of surfactant from polymer surface.

TABLE I
Amount of Surfactant Chemically Bound on the Surface of Cellulose Ester
With and Without Drying the Polymer Surface after Hydrolysis

Polymer films	Reaction amounts (mol/cm ²)	
	Without drying	With drying
Cellulose acetate	2.26×10^{-9}	1.18×10^{-9}
Cellulose propionate	1.89×10^{-9}	1.06×10^{-9}



(a)



(b)

Fig. 4. Surface tension vs. $\cos \theta$ curves: (a) cellulose acetate and propionate before treatment (by solution of nonionic surfactant); (b) cellulose acetate (by solution of glycerin); (c) cellulose propionate (by solution of glycerin).

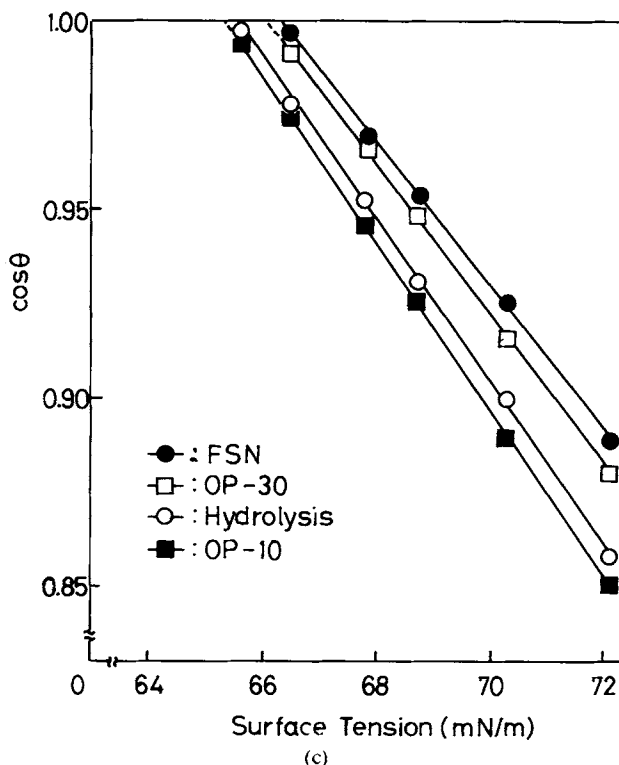


Fig. 4. (Continued from the previous page.)

The results of quantitative are shown in Table I. The density of surfactants fixed on the plate surfaces of cellulose esters was about twice as high as the density of hydroxyl groups on surface of cellulose (1×10^{-9} mol/cm²). This value suggests that two molecules of surfactants bind to one molecule of cyanuric chloride as shown in Figure 1 and also this small value shows that the surfactant molecules are fixed sparsely on the plate surface spaces wide enough to let water droplets seep into the plate surface exist among the fixed surfactants on the plate surface.

The density of fixed surfactants on the surface dried in vacuum after hydrolysis was small compared with that of the fixed surfactant on the wet

TABLE II
Critical Surface Tension of Cellulose Ester

Reaction step	Critical surface tension (mN/m)			
	Cellulose acetate		Cellulose propionate	
	Initial value	Set in vapor of 40°C for 10 days	Initial value	Set in vapor of 40°C for 10 days
Before hydrolysis	32.1	—	29.6	—
After hydrolysis	66.5	64.4	65.5	62.6
After reaction with FSN	68.5	68.3	66.3	65.3
After reaction with OP-10	66.2	65.7	65.3	63.5
After reaction with OP-30	68.0	67.2	66.1	64.1

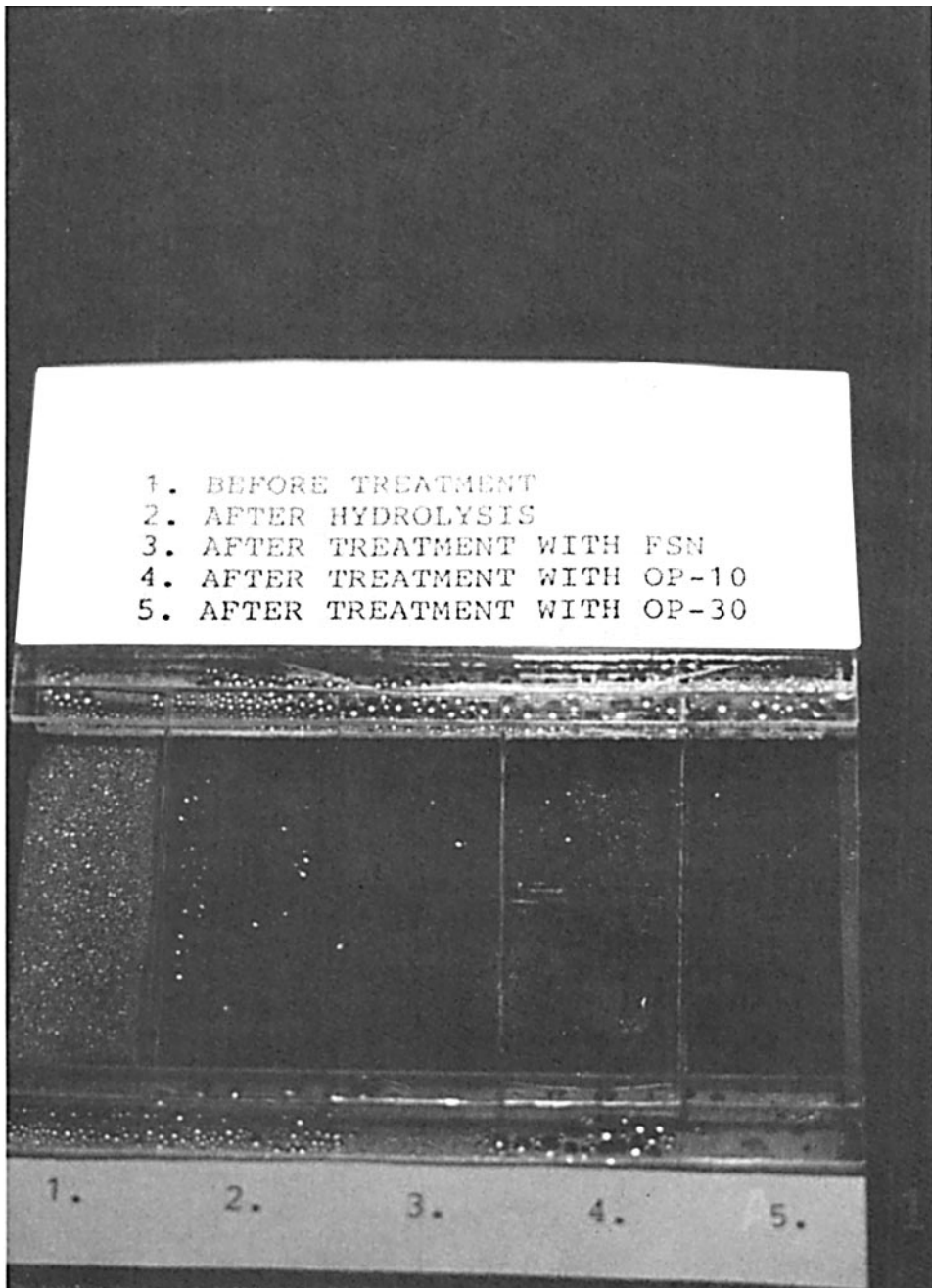


Fig. 5. Photograph of antifogging effect for surfaces of cellulose ester after treatment.

plate after hydrolysis. This difference suggests that hydrolysis hydroxyl groups exposed on the surface migrate inside the polymer plate by drying the surface after hydrolysis and the number of hydroxyl groups on the surface decrease.

Critical Surface Tension Measurements

Contact angles vs. surface tension curves for the plate surface of cellulose acetate and propionate are shown in Figures 4(a), 4(b), and 4(c), respectively. These curves shifted toward the decrease of $\cos \theta$ value in the order of OP-10, hydrolysis, OP-30, and FSN, respectively. This shows that some differences in the wettability exist exactly among the plates, although the γ_c obtained from Figures 4(b) and 4(c), as listed in Table II, are close to each other. The decreases of the wettability were in the orders of FSN > OP-30 > hydrolysis > OP-10. The surface after reaction with FSN showed the most excellent. The values of γ_c for cellulose ester plates set in the closed chamber filled with water vapor at 40°C for 10 days are also listed in Table II. The results show that the wettability of the plate after hydrolysis recedes. This may be due to some surface contamination after hydrolysis. From the value of γ_c for the plate with FSN on the surface, the plate was confirmed to have excellent wettability.

Antifogging Property

The photographs of the plate surfaces set in water vapor at 60°C are shown in Figure 5. As shown in this picture, obvious differences among the plate surfaces were observed. The plate surface before the reaction completely fogged, but the surfaces after reaction with FSN and OP-30 were almost clear. The plate surfaces after hydrolysis and with OP-10 began to fog at the same time. Both the plate surfaces with FSN and OP-30 showed almost the same wettability during a short period of time (a few days). However, during a longer period (about 1 year or more), the plate surface with FSN showed a much more excellent antifogging effect than that with OP-30. This can be explained by the following reasons: The fluorocarbon chains of FSN in the fixed surfactants may prevent migration of the surfactant molecules inside the polymer plate due to the water-repellent property and also furthermore the contamination of the plates from oily substances and the deposition of water droplets.

CONCLUSIONS

As shown in Figure 1, the surface of cellulose ester films treated chemically with FSN have a double structure consisting of a fluorocarbon chain corresponding to low surface energy and an ethylene oxide chain corresponding to high energy region. These fluorocarbon surfactants are fixed sparsely on the plate surface, and so are packed loosely without compact orientation. The fluorocarbon chains may contribute to the resistance to fogging due to water droplets, and also to the migration of the surfactant molecule into the polymer plate. As fluorocarbon chains have an excellent oil-repellent effect in comparison with the chain in hydrocarbon surfactants, the surfaces are not

apt to be contaminated by oil, etc. This would be one important factor in facilitation of the antifogging effect. On the other hand, the ethyleneoxide chain contributes to the spreading of water droplets.

Consequently, the antifogging effect was confirmed to be given fully by fixing the fluorocarbon nonionic surfactant on the plate surface of cellulose ester.

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