

Interaction of Cellulose with Small Molecules. Glycerol and Ethylene Carbonate*

ERIC WELLISCH, LAMONT HAGAN, LEON MARKER, and ORVILLE J. SWEETING

Film Division, Olin Mathieson Chemical Corporation, New Haven, Connecticut

INTRODUCTION

It has been of considerable theoretical as well as practical interest to understand the interactions of cellulose chains with each other and with small molecules such as water, glycerol, glycols, polyethers, amines, or other compounds which are capable of forming hydrogen bonds with the cellulosic structure. These types of compounds are used in appropriate circumstances commercially as *softeners* for cellophane, and are a major factor in determining the final mechanical properties.

In previous work^{1,2} we have shown that a freshly gelled cellulosic film (i.e., one regenerated from viscose without having been dried) absorbs glycerol from an aqueous solution principally by an exchange of water for glycerol solution. The aqueous softener within the sheet of cellulose has a concentration equal to or very close to the concentration of the softener bath through which it has passed. Enrichment in softener does not occur to any appreciable extent up to 95% of glycerol in the bath.

Only when water is expelled and the film begins to collapse during drying does the softener begin to interact with cellulose. This interaction begins at almost 95% R.H. (corresponding to 50-70% moisture content) and increases as the softener displaces water down to a moisture content of 6-9%. The dried base sheet then contains only tightly held water and softener solvating and screening the cellulosic hydroxyl groups. The interaction between softener and cellulose prevents interchain hydrogen bondings and is therefore believed to be a necessary condition for proper plasticization of cellulose.

Depending upon the affinity of the softener for cellulosic hydroxyls and upon the conditions of

drying, some change in accessibility may occur; essentially, however, the softening process can be considered as one of competitive exchange of water for softener at the cellulosic hydroxyl sites without any appreciable change in the amorphous to crystalline ratio of the base sheet.†

When gel cellophane is softened with various concentrations of glycerol ranging from zero to 80% glycerol and its volume is measured and compared with the sum of the volume of dry cellulose plus glycerol solutions measured separately, a constant contraction in volume of 0.80% is observed.³ This constant contraction, independent of glycerol concentrations, suggests that the interaction between cellulose and water and between cellulose and glycerol is similar, without appreciable change in the accessibility of cellulose.

If, therefore, the accessibility of cellulose is considered constant while in a state of collapse (between 70 and 5% water content), the cellulose-softener-water system may be regarded as a binary system of water and softener which should obey Raoult's Law. Deviations from Raoult's Law should give an indication of the interaction of the softener and water with cellulosic hydroxyl groups.

We can therefore attempt to express the softening process in terms of the interaction of water by considering and comparing only the following three systems.

(1) The cellulose-water system: this gives a measure of the affinity of water for cellulosic hydroxyl groups.

(2) The water-softener system: this establishes the affinity of water for the softener by measure-

† Note added in proof: Recently confirmation of the assumption made here (that softeners do not penetrate the crystalline regions) has been found in the work of Lyness and McKeown (*Abstr. of Papers, 137th Meeting Am. Chem. Soc., Cleveland, April 1960, p. 2E*), who have shown that no change occurs in the ratio of crystalline to amorphous cellulose, even under the more drastic conditions of hydrolysis.

*This work was presented at the 137th National Meeting of the American Chemical Society held at Cleveland in April 1960.

ment of the deviation from Raoult's Law. A standard is provided by which to measure the softener-cellulose interaction.

(3) The cellulose-water-softener system: this gives an indication of the interaction of the softener and cellulose in comparison to water and cellulose.

To determine the cellulose-softener interaction quantitatively it is assumed that any interaction between softener and cellulose will neutralize or inactivate the hygroscopic functional groups of both softener and base sheet in such a way that the reduction in moisture content of a softened film in comparison to the equilibrium moisture content of softener plus unsoftened cellulose is a direct measure of this interaction.

Let α represent the equilibrium moisture content of cellulose (which depends upon relative humidity), β represent the equilibrium moisture content of the softener (i.e., a measure of its hygroscopic nature), and γ represent the equilibrium moisture content of softened cellulose at any given relative humidity (which depends upon the nature of the small softener molecule, its concentration in the sheet, and the prevailing relative humidity). These three quantities may be readily determined experimentally, and from them can be calculated δ , the reduction in equilibrium moisture content that can be ascribed to cellulose-softener interactions. Thus δ is the deviation from additivity, defined as $\delta = \alpha + \beta - \gamma$.

EXPERIMENTAL

EQUILIBRIUM MOISTURE CONTENT AND SOFTENER CONCENTRATION

To obtain the interaction data, the equilibrium moisture contents of films containing a hygroscopic softener, such as glycerol, and films containing a nonhygroscopic softener, such as ethylene carbonate, were determined at several relative humidities and at softener concentrations between 10 and 30% softener in the film. Those values were compared with the equilibrium moisture content of unsoftened film and with the moisture content of pure softener at the same concentrations and relative humidities.

Equilibrium Moisture Content of Softeners

The equilibrium moisture content of the softeners was determined by permitting aqueous softener solutions to reach equilibrium at constant relative humidity. The attainment of equilibrium was followed by measuring the refractive index of the

solution until the refractive index remained constant for at least 48 hr. Softener solutions containing 5, 15, and 50% water were prepared and allowed to reach equilibrium at 15, 35, and 81% R.H., respectively. Refractive indexes were measured every 48 hr. until all solutions had reached constant moisture content.

To carry out these measurements calibration curves of refractive index as a function of moisture content were constructed. A nearly linear relationship exists to correlate refractive index with moisture content.

The softeners reached equilibrium moisture content after approximately 359 hr. At 15% R.H., glycerol had a water content of 9.2% and a refractive index (D line at 24°C.) of 1.4600; at 35% R.H., 14.4% water, n_D^{24} was 1.4532; and at 81% R.H., 43.6% water, n_D^{24} was 1.3930. The corresponding values for ethylene carbonate were 5.3% water and n_D^{24} 1.4179 at 81% R.H. (ethylene carbonate is a solid at 15 and 35% R.H.). (The water content for each softener solution has been corrected for the initial moisture content of the softener, as determined by Karl Fischer analysis.)

Table I presents the calibration data from which the curves relating water content and refractive index were constructed.

TABLE I
Refractive Index of Aqueous Solutions

Glycerol		Ethylene carbonate	
H ₂ O, %	n_D^{24}	H ₂ O, %	n_D^{24}
5.44	1.4652	0.00	Solid
10.17	1.4590	4.62	1.4186
14.90	1.4530	8.95	1.4152
19.63	1.4448	12.84	1.4102
33.74	1.4230	16.43	1.4068
38.47	1.4180	19.71	1.4039
43.20	1.4100		
47.94	1.4032		
52.67	1.3960		

Determinations of Equilibrium Moisture Content of Softened and Unsoftened Films at Various Relative Humidities

Unsoftened and softened cellophanes of known initial moisture and softener content (as determined by analysis) were cut with a template to obtain specimens 2.25 × 2.75 inches. The equilibrium moisture content of these specimens was determined at 15, 35, 65, 81, and 93% R.H. The gain in weight from water pickup was measured with a sensitive beryllium-copper spring calibrated to

read spring extension in milligrams to within ± 1 mg. by use of a cathetometer.

To avoid softener loss during conditioning insofar as possible, each film sample was conditioned inside a 32-oz. glass bottle containing 150–200 ml. of a humectant solution to give the desired relative humidity. The following saturated salt solutions were used as the humectant for unsoftened films: potassium nitrate for 93% R.H., ammonium

sulfate for 81% R.H., sodium nitrate for 65% R.H., magnesium chloride for 35% R.H., and lithium chloride for 15% R.H.

For softened films, humectant solutions were prepared with the same softener as contained in the film. The softener concentrations required for each softener type and relative humidity were determined from the moisture content determined by Karl Fischer analysis at equilibrium. For glycerol, these values were 7.4, 12.6, 30.0, 47.0, and 70% water at 15, 35, 65, 81, and 93% R.H., respectively; the corresponding values for ethylene carbonate were 0.2, 1.5, 4.0, 7.5, and 22.1% water. The gain in moisture content was measured every hour by the calibrated spring balance, and equilibrium was considered to have been reached when constant weight was attained. A typical measurement of equilibrium moisture content is given in Table II for a glycerol-softened film at 93% R.H.

TABLE II
Determination of Equilibrium Moisture Content of Glycerol-Softened Cellophane at 93% R.H.^a

Spring extension, cm.	Time, hr.	Weight, g.	Weight of water, g.	Water, % ^b
0.77 (wire alone)		0.048		
3.50 (wire and film)	0	0.215	0.0097	7.5
3.90	1.3	0.240	0.0347	26.7
3.96	2.1	0.242	0.0367	28.2
4.10	3.0	0.251	0.0457	35.2
4.19	3.8	0.259	0.0537	41.3
4.31	4.5	0.265	0.0597	46.0
4.73	20.8	0.290	0.0847	65.2
4.73	28.3	0.290	0.0847	65.2

^a By chemical analysis, initial H₂O = 5.82%; glycerol = 16.3%. Initial sample weight (0 hr.) by spring extension = 0.167 g. Then initial moisture in sample is 5.82% \times 0.167 = 0.0097 g.; initial softener in sample is 16.3% \times 0.167 = 0.0272 g. Cellulose in sample is 0.167 - (0.0097 + 0.0272) = 0.130 g.

^b Based on dry cellulose.

Equilibrium Moisture Content as a Function of Softener Concentration at Various Relative Humidities

The equilibrium moisture content of films softened with glycerol and ethylene carbonate was determined at 15, 35, 65, 81, and 93% R.H. for softener concentrations varying from about 5 to 40% softener content in the film based on dry cellulose. The softened films were prepared from gel film impregnated with softener solutions ranging from 5 to 20% bath concentration in 5% increments. The films were held in embroidery hoops

TABLE III
Equilibrium Moisture Content of Softened and Unsoftened Films and Corresponding $\alpha + \beta$ Values

Softener concentration in film, %	15% R.H.		35% R.H.		65% R.H.		81% R.H.		93% R.H.	
	H ₂ O, %	$\alpha + \beta$, %	H ₂ O, %	$\alpha + \beta$, %	H ₂ O, %	$\alpha + \beta$, %	H ₂ O, %	$\alpha + \beta$, %	H ₂ O, %	$\alpha + \beta$, %
Glycerol										
0.0	4.9	4.9	8.2	8.2	12.5	12.5	17.2	17.2	21.9	21.9
4.3	3.8	5.0	7.4	9.0	11.6	14.0	17.1	20.7	20.1	32.4
13.1	3.4	5.4	6.6	10.6	12.0	17.2	21.8	27.6	41.7	54.0
19.3	3.3	5.6	6.8	11.5	13.1	19.0	24.7	32.3	55.1	69.1
32.2	3.4	6.0	8.1	13.9	16.1	23.8	35.0	42.1	84.5	100.9
Ethylene carbonate										
0.0	3.1	3.1	5.4	5.4	10.8	10.8	12.8	12.8	20.6	20.6
13.7	11.0	3.1	21.6	5.4	30.2	11.1	29.6	13.4	45.4	22.2
20.9	10.8	3.1	19.8	5.5		11.2	29.2	13.8	46.3	23.2
32.6	11.3	3.2	21.6	5.5	30.2	11.5	28.7	14.4	47.9	24.3
44.8	10.8	3.2	20.7	5.5		11.7	28.6	15.0	49.7	25.7

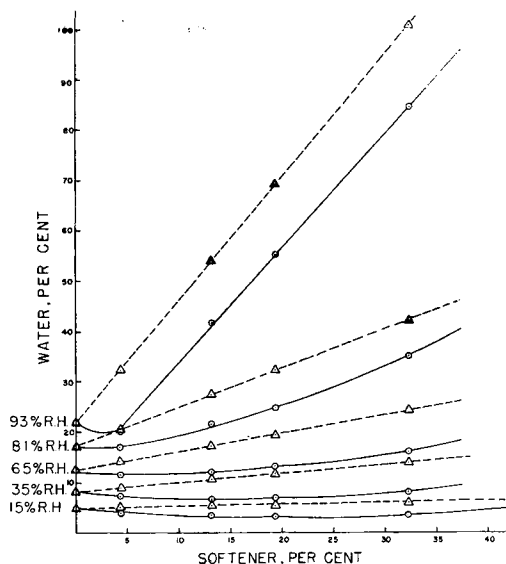


Fig. 1. Equilibrium moisture content and softener concentration of films softened with glycerol: (—) experimental points; (---) $(\alpha + \beta)$ values.

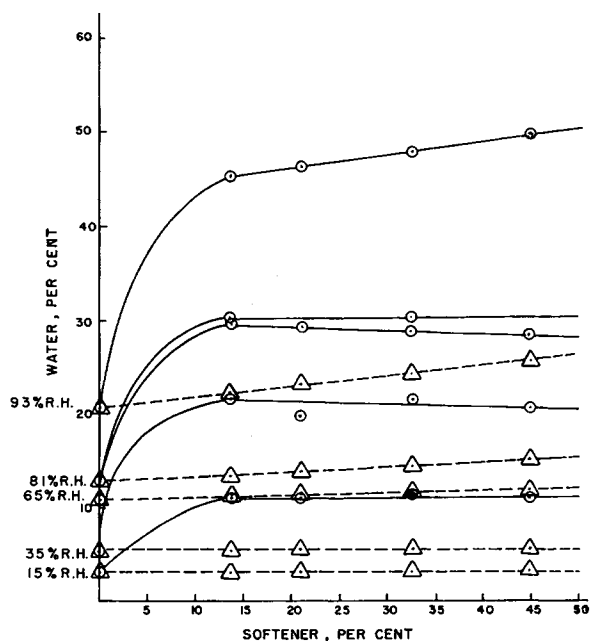


Fig. 2. Equilibrium moisture content and softener concentration of films softened with ethylene carbonate: (—) experimental points; (---) $(\alpha + \beta)$ values.

and kept in the impregnating bath (1-liter solutions) for 5 to 10 min., then dried at 110°C. for 90–100 seconds to keep the moisture content constant and as close as possible to 6–8%. The films were then analyzed for initial softener and moisture content, and their equilibrium moisture content was determined on the moisture balance.

Unsoftened control films were prepared at the same time.

The data obtained are given in Table III. The calculated $(\alpha + \beta)$ values from the pure softeners and unsoftened films are also shown. From these data Figures 1 and 2 were constructed.

Table IV is intended to summarize on a comparable basis the equilibrium moisture content of films prepared as already described and the sum of the α and β values for unsoftened sheets and the pure softeners. The values given are interpolated from Figures 1 and 2. All concentrations are based on 100 g. of dry cellulose. Only the lowest and highest concentrations were used to calculate the cellulose–softener interaction.

TABLE IV
Equilibrium Moisture Content for Softened and Unsoftened Films and for Pure Softeners

Softener in film	Softener concn., %	Equilibrium moisture content, %				
		15% R.H.	35% R.H.	65% R.H.	81% R.H.	93% R.H.
Glycerol	0	4.9	8.2	12.5	17.2	21.9
	10	3.4	6.8	11.6	19.7	33.0
	30	3.4	8.0	15.4	31.5	78.5
$\alpha + \beta$ values	10	5.3	9.9	15.9	24.9	46.8
	30	6.2	13.5	23.0	40.3	94.5
Ethylene carbonate	0	3.1	5.4	10.8	12.8	20.6
	10	11.0	21.0	30.2	30.0	44.8
	30	11.0	21.0	30.2	30.0	47.5
$\alpha + \beta$ values	10	3.1	5.4	10.9	13.2	21.7
	30	3.1	5.5	11.4	14.2	23.9

Since the reduction in water content of softened cellulose is the result of competitive interactions among cellulose, softener, and water, the equilibrium moisture data were converted (a) to mole fractions of water per moles of water plus moles of softener and (b) to mole fractions of water per moles of cellulose, softener, and water.

Water–Softener System

The mole fractions of water for the water–softener system are given in Table V and are plotted in Figures 3 and 4. These graphs of relative humidity as a function of mole fraction of water [per moles of water and softener associated with 100 g. (0.62 mole) of cellulose] show an abrupt break in the curves corresponding to the water sorption by primary hydroxyl groups of cellulose of about 50%

TABLE V
Mole Fractions of Water in the Water-Softener System per 100 g. of Cellulose

Softener in film	Softener concn., %	Water, mole fractions/100 g. cellulose				
		15% R.H.	35% R.H.	65% R.H.	81% R.H.	93% R.H.
Glycerol	0	0.303	0.424	0.528	0.606	0.663
	10	0.635	0.777	0.856	0.910	0.944
	30	0.360	0.570	0.720	0.840	0.930
Ethylene carbonate	0	0.21	0.33	0.49	0.53	0.65
	10	0.84	0.91	0.94	0.94	0.96
	30	0.64	0.77	0.83	0.83	0.88

crystallinity. This water of hydration appears to be affected also by the softener type and concentration, as shown in Table VI (which gives the number of moles of water held by 100 g. of cellulose in the presence of various amounts of glycerol or ethylene carbonate, read from Figures 3 and 4 at the intersections of the extrapolated lines). (The control films in Figures 3 and 4 express mole fractions of water associated with 0.62 moles of cellulose.) The data for glycerol show a decrease in the amount of water associated with the primary hydroxyl group of cellulose with increasing softener concentration in comparison to unsoftened film in which (at 50% crystallinity) about one mole of water is associated with one mole of primary

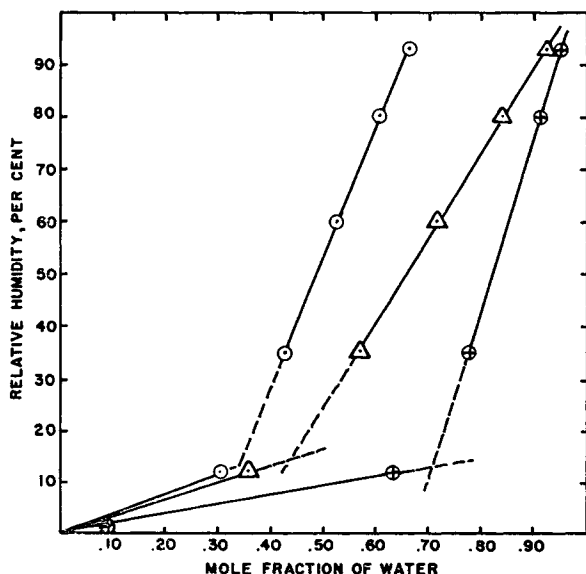


Fig. 3. Relative humidity as a function of mole fraction of water in the system, glycerol-water: (○) control film; (△) 30% glycerol; (⊕) 10% glycerol.

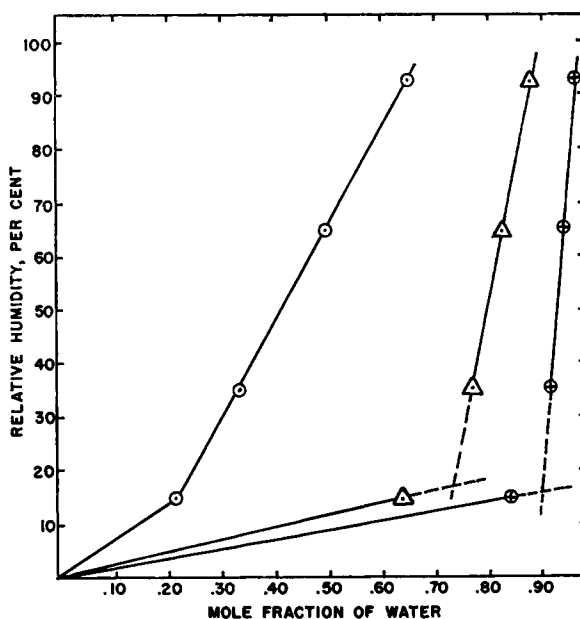


Fig. 4. Relative humidity as a function of mole fraction of water in the system, water-ethylene carbonate: (○) control film; (△) 30% ethylene carbonate; (⊕) 10% ethylene carbonate.

hydroxyl groups of cellulose. This must be caused by the strong affinity of glycerol for cellulose.

The large amount of water associated with cellulose softened with ethylene carbonate corresponds to hydration of all three hydroxyl groups and can be explained by the nonhygroscopic character of the compound which does not interact with cellulose but makes all hydroxyl groups accessible to water molecules.

Figures 3 and 4 show a linear relationship between vapor pressure and moisture uptake for glycerol and for ethylene carbonate, indicating no

TABLE VI
Moles of Water in the Water-Softener System per 100 g. of Cellulose (Intersection Values of Figures 3 and 4)

Softener	Softener concn., %	H ₂ O, mole fraction	Water concn., moles/100 g. cellulose	Relative humidity, %
Glycerol	0	0.340	0.319	13.0
	10	0.715	0.273	13.5
	30	0.445	0.262	14.5
Ethylene carbonate	0 ^a	0.230	0.185	16.0
	10	0.895	0.970	16.0
	30	0.740	0.970	18.5

^a Overdried film.

further softener-cellulose interaction between 35 and 93% R.H.

Cellulose-Water-Softener System

To consider the total cellulose-water-softener system we converted the data of Table IV to mole fractions of water per moles of water, softener, and cellulose, correcting for the water of hydration associated with primary hydroxyl groups. The mole fraction data are given in Table VII and are plotted as a function of relative humidity in Figures 5 and 6.

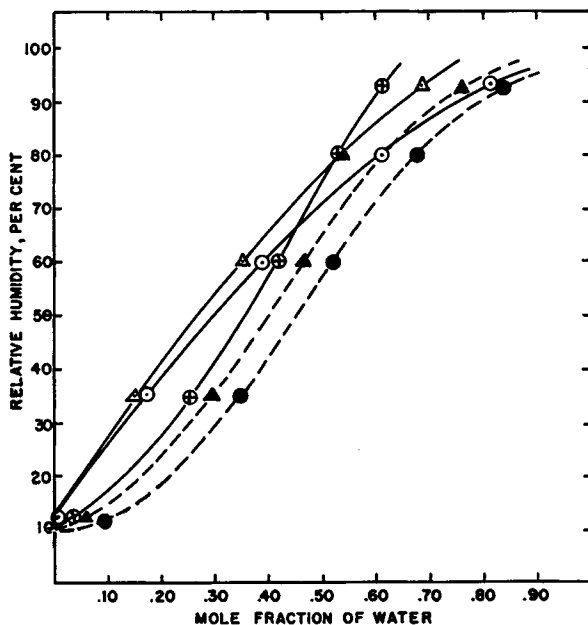


Fig. 5. Relative humidity as a function of mole fraction of water in the system; water-glycerol-cellulose: (⊕) unsoftened film; (Δ) 10% glycerol; (⊙) 30% glycerol. Broken lines are $(\alpha + \beta)$ values from Table VII: (▲) 10% glycerol; (●) 30% glycerol.

The plotted data show the following results. (1) The interaction of glycerol is strong at low humidities but decreases at higher relative humidities; apparently water is able to displace the softener as the mole fraction of water is increased. Softener at 30% concentration does not interact much more than softener at 10% and constitutes an excess. (2) The interaction of ethylene carbonate is negative and constant between 35 and 81% R.H. More water is absorbed at all humidities in comparison to unsoftened film, since the presence of this material prevents the interaction between cellulosic hydroxyl groups while no interaction with ethylene carbonate takes place.

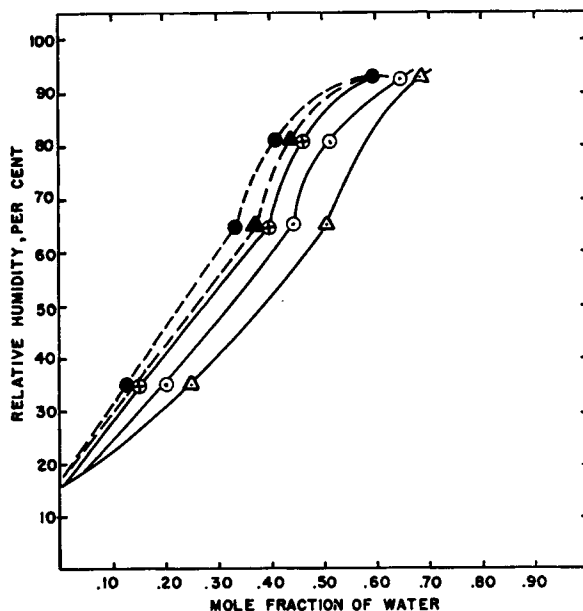


Fig. 6. Relative humidity as a function of mole fraction of water in the system; water-ethylene carbonate-cellulose: (⊕) unsoftened film; (Δ) 10% ethylene carbonate; (⊙) 30% ethylene carbonate. Broken lines are $(\alpha + \beta)$ values from Table VII: (▲) 10% ethylene carbonate; (●) 30% ethylene carbonate.

TABLE VII
Cellulose-Water-Softener System: Mole Fractions of Water*

Softener in films	Softener concn., %	Water, mole fraction				
		15% R.H.	35% R.H.	65% R.H.	81% R.H.	93% R.H.
Glycerol	0	0.033	0.250	0.417	0.530	0.610
	10		0.151	0.354	0.538	0.684
	30		0.170	0.390	0.613	0.813
$\alpha + \beta$ values	10	0.057	0.295	0.465	0.610	0.762
	30	0.090	0.346	0.519	0.678	0.841
Ethylene carbonate	0	0.151	0.398	0.456	0.605	0.681
	10	0.247	0.507	0.574	0.681	0.681
	30	0.200	0.438	0.505	0.640	0.640
$\alpha + \beta$ values	10	0.141	0.371	0.438	0.603	0.603
	30	0.127	0.333	0.407	0.597	0.597

* Corrected for water associated with the primary hydroxyl groups.

Interaction Values

The reduction in water content of these softened films caused by interaction as defined above was calculated as the difference in mole fractions using the data given in Table VII. These data were then converted to moles of water per moles of

TABLE VIII
Reduction in Water Content Caused by Interaction

Softener	Softener concn., %	δ values, moles water/moles softener and cellulose			
		35% R.H.	65% R.H.	81% R.H.	93% R.H.
Glycerol	10	0.17	0.12	0.08	0.08
	30	0.21	0.15	0.07	0.03
Ethylene carbonate	10	-0.12	-0.16	-0.16	-0.09
	30	-0.08	-0.12	-0.11	-0.05

softener and moles of cellulose (Table VIII) and give a quantitative measure of cellulose-softener interaction.

CONCLUSIONS

The interaction values show that the interaction between glycerol and cellulose is at a maximum at approximately 35% R.H. and decreases steadily with increasing equilibrium moisture content at the higher humidity conditions; the higher softener content causes additional interaction at 35 and 65% R.H., but at 81 and 93% R.H. water is capable of displacing the softener at the cellulosic hydroxyl sites.

The nonhygroscopic ethylene carbonate shows an almost constant and negative interaction at all humidities. This compound apparently acts only as an inert cushion between cellulose chains permitting complete cellulose-water interaction. At the higher concentrations the water-repellent effect of this compound decreases the magnitude of this repulsion. The presence of a nonhygroscopic molecule which shows negative interaction leads eventually to crosslinking of cellulose chains, as the material is easily lost, and finally results in embrittled film of poor durability.

References

1. Sweeting, O. J., R. Mykolajewycz, E. Wellisch, and R. N. Lewis, *J. Appl. Polymer Sci.*, **1**, 356 (1959).
2. Mykolajewycz, R., E. Wellisch, R. N. Lewis, and O. J. Sweeting, *J. Appl. Polymer Sci.*, **2**, 236 (1959).
3. Unpublished results obtained in this laboratory.

Synopsis

The equilibrium moisture content of films softened with hygroscopic glycerol or nonhygroscopic ethylene carbonate was determined as a function of softener concentration at

15, 35, 65, 81, and 93% R.H. and compared to the hygroscopicity of unsoftened film and of the pure softeners at the same concentrations. The difference in water content assumed to be caused by interaction between softener and cellulose was calculated in moles of water per mole of softener and per mole of cellulose. A quantitative measure of softener-cellulose interaction at low and high relative humidities is thus obtained. Ethylene carbonate shows a negative interaction and seems to function only as an inert cushion between cellulose chains, while glycerol interacts with cellulose. This interaction increases with decreasing moisture content (at lower relative humidities) and with increased softener concentration. The softener-cellulose interaction is a necessary condition for proper softening.

Résumé

On a déterminé l'équilibre à l'humidité des films plastifiés avec de la glycérine hygroscopique ou du carbonate d'éthylène non-hygroscopique en fonction de la concentration en émoulliant à 15, 35, 65, 81, et 93% d'humidité relative et on le compare à l'hygroscopicité du film non plastifié et celle des émoulliants purs aux mêmes concentrations. On a calculé la différence dans la teneur en eau, présumée due à l'interaction entre le plastifiant et la cellulose en moles d'eau par môle de plastifiant et par môle de cellulose. On obtient ainsi une mesure quantitative de l'interaction plastifiant cellulose à des humidités relatives faibles et élevées. Le carbonate d'éthylène montre une interaction négative et semble ne fonctionner que comme coussin inerte entre les chaînes de cellulose tandis que la glycérine réagit avec la cellulose. Cette interaction croît en raison inverse de la teneur en eau (pour des humidités relatives faibles) et en fonction directe de la concentration en plastifiant. L'interaction plastifiant cellulose est une condition nécessaire pour une plastification réelle.

Zusammenfassung

Der Gleichgewichts-Feuchtigkeitsgehalt von Filmen, die mit Glycerin als hygroscopischer, oder Äthylenkarbonat als nichthygroscopischer Substanz weichgemacht waren, wurde in Abhängigkeit von der Weichmacherkonzentration bei 15, 35, 65, 81 und 93% relativer Feuchtigkeit bestimmt und mit der Hygroscopicität der nicht weichgemachten Filme und der reinen Weichmacher bei der gleichen Konzentration verglichen. Der Unterschied im Wassergehalt, für den die Wechselwirkung zwischen Weichmacher und Cellulose verantwortlich gemacht wird, wurde als Mole Wasser pro Mol Weichmacher und pro Mol Cellulose berechnet. Es wird so ein quantitatives Mass für die Wechselwirkung zwischen Weichmacher und Cellulose bei niedriger und hoher relativer Feuchtigkeit erhalten. Äthylenkarbonat zeigt eine negative Wechselwirkung und scheint nur als inertes Polster zwischen den Celluloseketten zu fungieren, während Glycerin mit der Cellulose in Wechselwirkung tritt. Diese Wechselwirkung nimmt mit fallendem Feuchtigkeitsgehalt (bei niedrigerer relativer Feuchtigkeit) und mit erhöhtem Weichmachergehalt zu. Die Wechselwirkung zwischen Weichmacher und Cellulose ist eine notwendige Voraussetzung für eine eigentliche Weichmachung.

Received January 19, 1960