Preparation and Properties of Phenolated Corn Bran (CB)/Phenol/Formaldehyde Cocondensed Resin

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ABSTRACT: Corn bran (CB) was liquefied in the presence of phenol at high temperature (200°C) under high pressure (>1 atm) and the obtained liquefied products were reacted with formaldehyde to get phenolated CB/phenol/formaldehyde resins with excellent yields. The properties of the cocondensed resins were examined and compared with the liquefied products before the cocondensation. Little difference was observed in thermofluidity before and after the cocondensation, whereas the thermosetting properties and the flexural properties of the molded products were enhanced. These properties were comparable with those of liquefied resins from corn starch (CS) and those of commercial novolak resin. Moreover, no significant differences were found in the properties of the liquefied products and the thermosetting resins therefrom after removal of the solid residue and neutralization salt. It became apparent that the condensation reactions between formaldehyde and the unreacted phenol in the liquefied products enhance the physical properties of the liquefied products from CB, making possible the total utilization of the liquefied products. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2901–2907, 2000

Key words: corn bran; phenol; cocondensation resin; formaldehyde; thermosetting resin; liquefaction

INTRODUCTION

Studies on the liquefaction methods of lignocellulosic matter have been actively performed in recent years,[1–4] trying to find its effective utilization. Recently, a large concern has been to reduce CO_2 emission. In this concern, food industries, for instance, are trying to discover new technologies to utilize their biomass wastes. As one of these technologies, this liquefaction technology for biomass is considered meaningful in the effective utilization of them.

In a previous article, we reported that corn bran (CB), which is a byproduct of the corn starch (CS) process, can be liquefied in the presence of

phenol and an acid catalyst.[5] It was then demonstrated that biomass, containing small amounts of cellulose and lignin, can be effectively liquefied by the acid-catalyzed method generally utilized for the liquefaction of wood. Also, the thermofluidity of the obtained liquefied products and the flexural properties of the thermoset moldings therefrom are comparable to those of the commercial novolak resin and its moldings.

To liquefy CB completely, however, a large amount of phenol was required. Large portions of phenol remained in the liquefied product without chemical bonding to the depolymerized fragments of CB. The remaining unreacted phenol has usually been vacuum-distilled from the liquefied products, rendering the liquefaction process complex and energetically disadvantageous. Therefore, a process in which formaldehyde is added to the liquefied product and reacted with the resid-

ual free phenol can be proposed. Lin et al.[6] and Alma et al.[7] found that cocondensed products can be obtained among depolymerized wood components, unreacted phenol, and formaldehyde, as described later, and that the thermofluidity of the products and the flexural properties of the thermoset moldings are higher than those obtained from the liquefied wood without the cocondensation reaction. Moreover, for the preparation of the novolak resin, the reaction system should be acidic, and in this regard, it can be said that since the pH of the liquefied products prepared by the acid-catalyzed method is in the range of the strong acids no addition of acid is required. This is also one of the advantages of this cocondensation reaction.

In this study, we tried to cocondensed the unreacted free phenol with formaldehyde as a method for the total utilization of the liquefied products obtained from CB and for the further enhancement of the physical properties of the liquefied products and the final molded products therefrom. We also tried to avoid the removal of the residual solid biomass remaining in the liquefied products as well as the salt formed during the neutralization of acids with MgO. The effect of the presence of these materials within the liquefied product on its physical properties was examined. Furthermore, the liquefied products from CS were considered to be a closely related material, and their cocondensed resins have also been comparatively studied in regard to their reactivities and their physical and mechanical properties.

EXPERIMENTAL

Materials

The CB and CS used in the liquefaction were donated by Sanwa Starch Ltd Co. They were dried in an oven at 105°C for 24 h and then kept in a desiccator at room temperature before use. Both wood flour (200 mesh), used as a filler for molding, and a commercial novolac resin (Novolak, HP-700) were supplied by the Hitachi Chemical Co. Methanol, used for the measurement of the amount of combined phenol, was of HPLC grade, and tetrahydrofuran (THF), used as an eluting solvent for gel permeation chromatography (GPC), was of extra pure grade containing 0.03% of the stabilizer (2,6-di-*t*-butyl-4-methylphenol). All other chemicals, purchased from commercial sources, were of reagent grade.

Preparation of the Resins

The liquefaction of CB and CS was conducted by using sulfuric acid at 200°C under high pressure and at 150°C under atmosphere pressure, respectively. After liquefaction, the calculated amount of formalin (37% aqueous solution) was added into the liquefied products to maintain the mol ratio of unreacted phenol to formaldehyde at 1 : 0.8. A cocondensation reaction was conducted at 105°C under reflux. After a definite reaction time, the cocondensed mixtures were diluted with acetone and then neutralized by magnesium oxide (MgO). For making a condensed resin without a methanol-insoluble residue and the salt formed during the neutralization of acids with MgO, the cocondensed mixtures were filtrated through a glass fiber filter (Toyo GA100). Finally, the cocondensed mixtures were concentrated by pressure-reduced evaporation (about 20 mmHg) at 50 and 180°C to remove the diluting solvent and unreacted phenol, respectively.

Characterization of the Resins

The novolak yield of unreacted phenol remaining after liquefaction to a resin in the cocondensation reaction was calculated according to the following equation:

$$\text{Novolak resinification yield} = (UP_2 - UP_1)/UP_2$$

where UP_2 is the amount of unreacted phenol in the liquefied product, and UP_1, the amount of unreacted phenol in the cocondensed resin.

The molecular weight and the molecular weight dispersion of resins were determined using a gel permeation chromatograph equipped with a differential refractometer R401 detector. THF was used as the mobile phase at a flow rate of 1.0 mL/min with 7.0 MPa pressure. The concentration of the samples was 0.5 wt % in the THF solutions and the injecting amount for measurement was 150 μL. The molecular weights of the samples were calibrated by monodisperse polystyrene standards.

The thermofluidities of all the samples were measured by a flow tester CFT-500A (Shimazu) with a die having an orifice of 1 mm (diameter) and 10 mm length. The start temperature and heating rate were fixed to 50 and 10°C/min, respectively, to measure the flow temperature. The apparent melt viscosity was determined in the same apparatus at 130°C under a pressure of 5.0 MPa. A formulation containing 37.7 wt % resins,
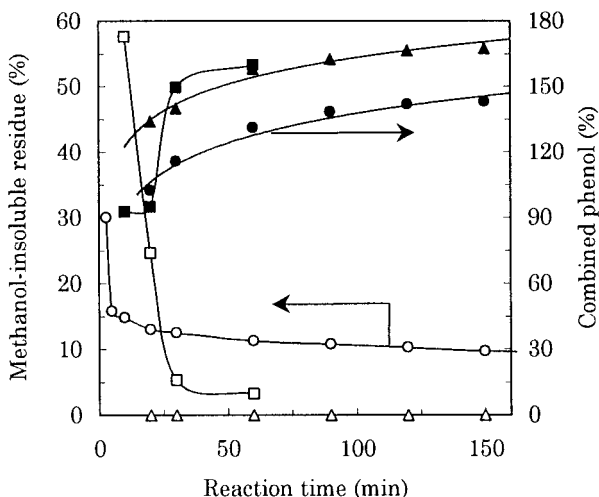
Figure 1 Effect of reaction time on the methanol-insoluble residue and combined phenol amount of phenolated CB and CS. Catalyst, 3%; phenol/CB or CS ratio, 3; (●,○) CB (150°C); (■,□) CB (200°C); (▲,△) CS (150°C).

9.4 wt % hexamine, 49.5 wt % wood fillers, 2.4 wt % calcium hydroxide, and 1.0 wt % zinc stearate was used to prepare molded specimens for mechanical tests. The obtained mixture was molded at 170–180°C under 50 MPa pressure for 5 min. The flexural properties of the molded specimens were measured by using an Autograph AGS-5kNG (Shimadzu). Flexural strength and elasticity modulus were calculated by the included Shikibu program, and flexural toughness was determined by the area under the stress–strain curve.

RESULTS AND DISCUSSION

As shown in Figure 1, the amount of the unliquefied CB (so-called CB residue) decreases and levels off at about 10%, within a short liquefaction period (20 min) at 150°C under atmospheric pressure. CS, used as a reference, could also proceed with its liquefaction smoothly at 150°C under the same atmospheric conditions. However, in this case, the amount of the unliquefied residue fell to 0% within the initial 20 min of reaction. On the other hand, when the liquefaction of CB was carried out in an autoclave under a more severe condition than the above, that is, at high temperature (200°C) and under a pressure (>1 atm) given by the vapor tension inside the reactor, the CB residue was lowered to less than 5% after a relatively short time (30 min). The amount of

combined phenol, obtained in that case, came to almost the same value as that attained in the CS liquefaction, that is, about 160% (Fig. 1). These facts suggest that the liquefaction of CB is significantly affected by the reaction temperature and pressure.

After getting the liquefied products from CB (at 200°C under high pressure) and CS (at 150°C under atmospheric pressure) and measuring the amount of unreacted free phenol, the obtained liquefied products were reacted with formaldehyde to get phenolated CB or CS/phenol/formaldehyde resins. The phenol resinification was performed under acidic conditions (as in novolak resin formation) by making use of the acid catalyst previously used for the liquefaction.

Typical resinification-time studies are shown in Figure 2, in which the starting conditions are 37.3 and 35.5% of unreacted free phenol for the liquefied products of CB and CS, respectively, and 150% of combined phenol for both liquefied products (see other reaction conditions in the Experimental section). As shown in this figure, both the decrease in the amount of unreacted free phenol and the increase in the novolak resinification yield level off within relatively short times: 80 min for CB and less than 20 min for CS. The level-off values of unreacted free phenol for CB and CS are 10 and 7%, respectively, and those of the novolak resinification yield for CB and CS are 72 and 80%, respectively. These values indicate that it is easier to decrease the unreacted phenol
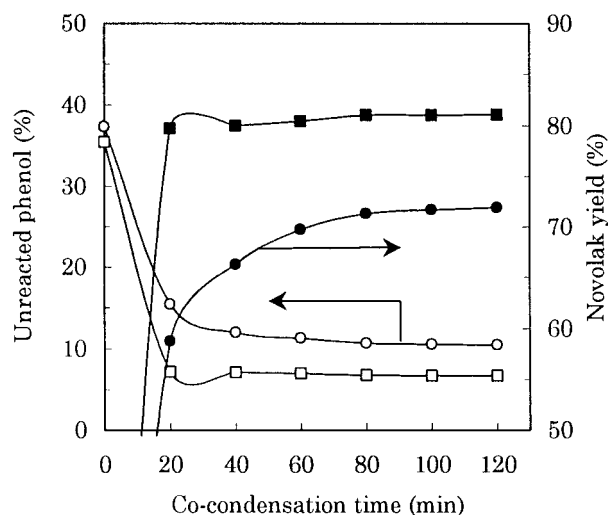

Figure 2 Effect of cocondensation time on the unreacted phenol and the novolak yield content of phenolated CB or CS/phenol/formaldehyde resin. Temperature, 105°C; unreacted phenol/formaldehyde molar ratio, 1/0.8; (●,○) CB; (■,□) CS.
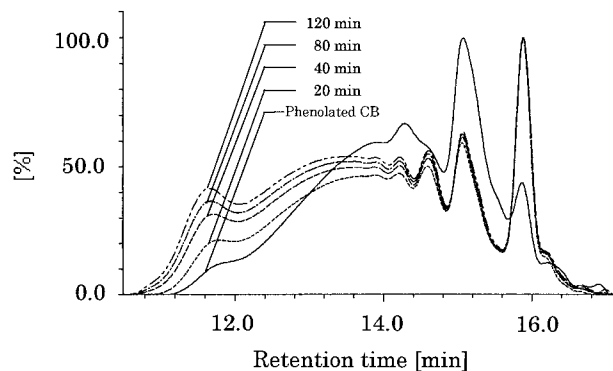
Figure 3 Effect of cocondensation time on the molecular distribution of phenolated CB/formaldehyde resin.

Figure 5 Effect of cocondensation time on the molecular weight and the molecular weight dispersion of phenolated CB and CS/formaldehyde resin. ($\bullet$,$\circ$) CB; ($\blacksquare$,$\square$) CS.

amount and to increase the novolak resinification yield in CS than in CB. One of the reasons is the difference in the acidity of the liquefied products; the pH values for CB and CS are 2.0 and 0.5, respectively. However, the obtained novolak resinification yielded more than 70%, revealing that the condensation reaction progressed satisfactorily.

Figures 3 and 4 illustrate the molecular distribution curves corresponding to different condensation periods for CB and CS, respectively. In both cases, the newly formed high molecular weight portion increased with the reaction time. The trends of the increase in the molecular weight is in good agreement with the above-mentioned experimental findings. In the CB case, the higher molecular weight portion increased steadily with the reaction period, whereas in the case of CS, a large increase in the high molecular weight portion was attained within the first 20 min, followed by a leveling off of the molecular weight. In Figure 5, the weight-average molecu-
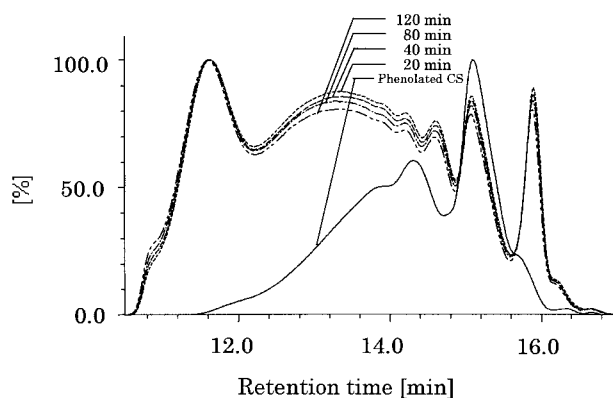

Figure 4 Effect of cocondensation time on the molecular distribution of phenolated CS/formaldehyde resin.
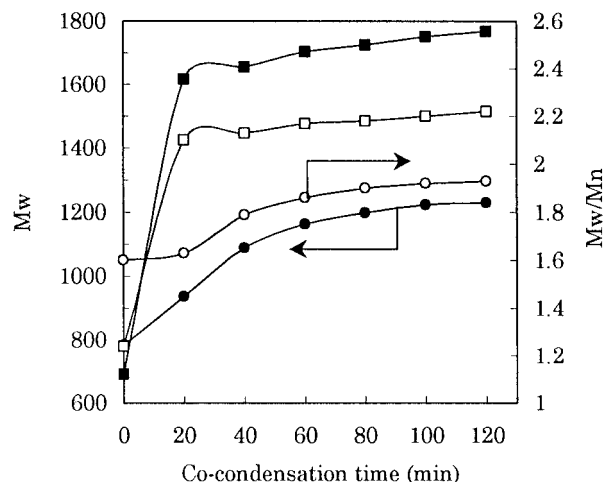
lar weight (M_w) and polydispersity were plotted as a function of the cocondensation time. M_w increased with the reaction time and leveled off at values that were 1.5 and 2 times larger for CB and CS, respectively, compared with those before the cocondensation. The polydispersity of the products increased also with the reaction time in both cases (Fig. 5).

The results of the characterization of the phenolated CB or CS/phenol/formaldehyde cocondensed resins are shown in Table I in comparison with those of phenolated CB or CS before cocondensation (liquefied CB or CS in the presence of phenol and an acidic catalyst). The thermal properties of the phenolated CB/phenol/formaldehyde cocondensed resin were almost identical to those of phenolated CB before the cocondensation. In the case of CS, even though a small increase in the flow temperature was detected, the cocondensation reaction did not have a large influence on the thermal properties of the products. Generally, an increase in the molecular weight of the liquefied products is known to worsen the thermomolding properties,[8] but the present results reveal scarcely the influence of the molecular weight increase on the thermofluidity caused by the cocondensation. Actually, Lin et al. and Alma et al. reported also the characteristics of the cocondensed resins obtained from liquefied wood, showing an improvement in their thermal properties.[6,7] It was also reported that improvement of the thermal properties of liquefied wood can be attained by blending with commercial novolak resin.[8] Thus, although there occurs a negative

Table I   Thermal Flow Properties of Phenolated CB or CS and Phenolated CB or CS/Phenol/Formaldehyde Cocondensed Resin

Sample	Cocondensation Time (min)	M_w	T_s[a] (°C)	T_f[b] (°C)	Melt Viscosity[c] (Poise)
Phenolated CB[d]	—	784	98.7	120.8	4629
Phenolated CB[e]	—	—	84.6	108.2	1302
Cocondensed resin[e]	20	937	95.2	118.3	4939
	80	1199	98.8	125.0	9104
	120	1230	97.5	123.7	5849
Phenolated CS[d]	—	691	79.5	100.0	467
Phenolated CS[e]	—	—	85.4	112.1	2484
Cocondensed resin[e]	20	1616	101.4	119.1	5047
	80	1725	97.5	122.5	7916
	120	1769	100.0	125.0	10960
Novolak	—	3814	90.3	110.0	—

[a] Softening temperature.
[b] Flow temperature.
[c] Measured at 130°C.
[d] Without residue and salt.
[e] With residue and salt.

effect caused by the increase in the molecular weight of the liquefied products, this effect can be compensated by the formation of novolaklike resins synthesized from the unreacted free phenol and formaldehyde.

After the liquefaction process, the acid used as the catalyst was neutralized, resulting in certain amounts of salt. The thermofluidity of the liquefied products, from which the salt as well as unliquefied CB residues were not separated, was investigated. The liquefied product containing such admixtures did not show a large difference when compared with that of the liquefied product free of admixtures. This result demonstrates that the liquefied products can be directly used without removing these solid by-products.

Figure 6 shows typical curing curves for resins obtained from the liquefied biomass. These curves result from the plotting of the torque as a function of the reaction time under constant pressure and strain. Generally, a standard parameter for describing the curing behavior of thermosetting resins is the time at which the torque of the resin attains 90% of its maximum value, so-called $Tc(90)$. The $Tc(90)$ values for different obtained samples are shown in Table II. It can be observed from this table that the curing advanced well for all the liquefied products at a curing temperature of 170°C. Among the $Tc(90)$ values, however, there are small differences. $Tc(90)$ values are slightly higher for the liquefied products before

the condensation reaction than for a commercial novolak resin. The novolak resinification yield increased with the condensation time, and the $Tc(90)$ values tend to decrease gradually with it. The values become comparable then to those of the commercial novolak resin. Some liquefied products showed higher thermosetting reactivities than that of the commercial novolak resin. From these results, it can be pointed out that the condensed materials yielded by the reaction between the unreacted free phenol remaining in the liquefied products and formaldehyde can enhance
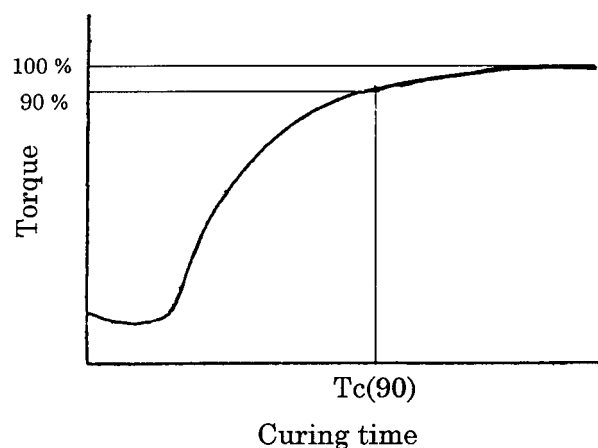

Figure 6 Curing curve of phenolated CB and CS/formaldehyde resin obtained by using a curelastometer.

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Table II Comparison of Curing Time of Phenolated CB or CS and Phenolated CB or CS/Phenol/Formaldehyde Cocondensed Resin

Sample	Cocondensation Time (min)	Novolak Resinification Yield (%)	$Tc(90)^a$
Phenolated CB[b]	0	—	1.87
Phenolated CB[c]	0	—	1.96
Cocondensed resin[c]	20	58.7	1.61
	80	71.3	1.52
	120	72.0	1.26
Phenolated CS[b]	0	—	1.82
Phenolated CS[c]	0	—	1.91
Cocondensed resin[c]	20	79.7	1.77
	80	81.0	1.44
	120	81.1	1.36
Novolak	—	—	1.74

[a] Curing time at 90% torque.
[b] Without residue and salt.
[c] With residue and salt.

the thermosetting reactivity of the cocondensed liquefied products.

Furthermore, when comparing the liquefied products with and without the neutralization salt and the unliquefied CB residue, the difference in the curing reactivity is small, showing that the presence of these admixtures does not affect significantly the thermosetting reactivity. Moreover, almost the same tendency was found when comparing to the liquefied products from CS. These facts confirm that the thermosetting resins can be prepared from CB-liquefied products, being comparable to the liquefied products from CS and to the commercial novolak resins in their thermocuring reactivities.

Thermosetting moldings were obtained by curing the liquefied products or the cocondensed liquefied products previously mixed with wood flour filler in a 50% amount. The flexural properties of these thermosetting moldings are shown in Table III. The thermosetting molding from the cocondensed liquefied products prepared by the reaction with formaldehyde for 120 min was found to have a flexural strength of 69 MPa, showing an enhancement of its flexural strength by the cocondensation reaction when compared to the flexural strength of 56 MPa for the liquefied product before the cocondensation. It is also noteworthy that the flexural strength value of 69 MPa for the thermosetting molding from the cocondensed liquefied product is fairly close to that of the thermosetting molding from novolak resin (86 MPa). In other words, the cocondensed CB liquefied

product is considered to be fairly practical. Moreover, not only was the flexural strength increased, but also the flexural modulus and the flexural toughness were enhanced by the cocondensation reaction.

On the other hand, when compared to the flexural properties of the thermosetting moldings from liquefied CS before and after cocondensation, the corresponding values for the CB were almost identical. Thus, it can be concluded that thermosetting moldings have flexural properties comparable to those from CS and commercial novolak resins can be obtained from the CB liquefied products. Furthermore, the influence of the presence of the unliquefied residue and the neutralization salt on the flexural properties of the thermosetting moldings was also examined, and almost no influence was recognized for both CB and CS. The same was also found in the flexural properties of the thermosetting moldings from the cocondensed liquefied products with or without the admixtures. These facts indicate clearly that the process for removing these admixtures can be avoided.

CONCLUSIONS

Phenolated CB/phenol/formaldehyde cocondensed resin could be prepared with high yields by a cocondensation reaction of the CB liquefied in the presence of phenol using the acid-catalyzed method and formaldehyde. The obtained cocon-

Table III   Flexural Properties of Phenolated CB or CS and Phenolated CB or CS/Phenol/Formaldehyde Cocondensed Resin

Sample	Cocondensation Time (min)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Flexural Toughness (MPa)
Phenolated CB[a]	—	56	8545	20
Cocondensed resin[a]	80	69	8202	31
Phenolated CB[b]	—	55	8814	19
Cocondensed resin[b]	20	61	8691	24
	80	66	8292	28
	120	69	8892	29
Phenolated CS[a]	—	61	7523	26
Cocondensed resin[a]	80	67	7396	33
Phenolated CS[b]	—	57	8817	20
Cocondensed resin[b]	20	64	7709	27
	80	64	8459	27
	120	71	8196	34
Novolak	—	86	9005	37

[a] Without residue and salt.
[b] With residue and salt. Molding: 170–180°C, 5 min, 5.0 MPa.

densed products were examined for their thermofluidity, thermosetting reactivity, and flexural properties of the thermosetting moldings prepared therefrom, and these properties were compared with those obtained for the liquefied products before condensation. It was known that the liquefied products before and after the condensation resemble each other in their thermofluidities and that the thermosetting reactivity and the flexural properties can be enhanced by the condensation. Furthermore, it is known that these properties are comparable to those for the CS liquefied products and commercial novolak resin. Thus, it can be considered that the condensation of the unreacted free phenol within the CB liquefied product with formaldehyde plays an important role in the effective utilization of the liquefied products from CB. The comparison of the liquefied products and their thermosetting moldings with or without removal of the unliquefied residue and the neutralization salt showed that these admixtures had no effect on thermofluidity and flexural properties. This result has considerable importance from the viewpoint of setting up a liquefaction process that is simple and economical.

As a conclusion, it can be said that from the acid-catalyzed liquefaction products of CB and their cocondensation products with formaldehyde three-dimensionally curable resins are obtainable, their properties being comparable to the same liquefied products from CS and commercial novolak resin. Therefore, this type of liquefaction method can be readily applied to biomass other than lignocellulosics. The present work should be considered as the first step of a further development of novel materials from all the biomass including agriculture-production wastes, food industry waste, and others.

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