

The Effect of Precipitation on the Molecular Weight Distribution of Cellulose Tricarbanilate

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Synopsis

The effect of precipitation on the molecular weight distributions of cellulose tricarbanilate (CTC) samples prepared from α -pulp, hydrolyzed α -pulp, and Avicel was determined using size exclusion chromatography (SEC). Precipitation of the CTC samples in methanol resulted in the loss of a low molecular weight fraction accounting for 26% of the weight of the hydrolyzed α -pulp, 20% of the Avicel, and 5% of the α -pulp. Precipitation in a methanol/water mixture resulted in less fractionation; in this case, however, the reaction byproducts were also precipitated. These results indicate that the molecular weight distribution of precipitated CTC may not accurately reflect the molecular weight distribution of the original cellulose. SEC analysis of the nonvolatile products from the carbanilation reaction offers a simple method for determining the complete molecular weight distribution of this cellulose derivative.

INTRODUCTION

Size exclusion chromatography (SEC) is widely used to obtain the molecular weight distribution of polymers. Since the physical properties of polymeric materials depend on the molecular weight distribution (MWD) of the constituent polymer, SEC is a valuable tool for quality and process control in the polymer industry.

SEC has been used to determine the MWD of cellulose from different sources¹⁻⁴ and to follow changes in the MWD of cellulose during chemical treatment.⁵⁻⁷ Since cellulose is not soluble in the organic solvents normally used for SEC, samples must be derivatized prior to analysis. The carbanilate derivative of cellulose is often employed because this derivatization procedure leads to trisubstitution of the cellulose and is not degradative.⁸ The MWD of the cellulose tricarbanilate (CTC) derivative is thus representative of the MWD of the original cellulose and its SEC separation is due solely to differences in molecular weight and not to the degree of substitution.

The usual method for cellulose tricarbanilate preparation is to react the cellulose with phenyl isocyanate using pyridine as both a solvent and a catalyst.⁸⁻¹⁰ The CTC is recovered from the pyridine solution and separated from the reaction byproducts by precipitation in a nonsolvent. For example, Valtasaari and Saarela⁹ precipitated their CTC samples by adding the pyridine solutions to 5-10 times their volume of methanol. Schroeder and Haigh¹⁰ first diluted the pyridine solution with 10-20% dioxane, and then precipi-

tated the CTC in a methanol/acetic acid mixture. Ashmawy et al.³ used absolute ethanol to recover the CTC from solution.

For the MWD of the precipitated CTC to reflect the original MWD of the cellulose, the precipitation procedure must not fractionate the sample. Sutter and Burchard¹¹ have noted that CTC oligomers cannot be precipitated in methanol. Therefore, the MWD of precipitated CTC samples may not be representative of the MWD of the original cellulose if the cellulose contains a low molecular weight fraction. By analyzing the entire reaction mixture from the carbanilation procedure, it has been possible to show that the results of the CTC precipitation process do not accurately reflect the appearance of the MWD of the original cellulose sample.

EXPERIMENTAL

Materials

The cellulose samples included α -pulp, hydrolyzed α -pulp, and Avicel. The hydrolyzed α -pulp was prepared by refluxing α -pulp in 2.5*N* HCl for 30 min. The hydrolysis residue was washed thoroughly, first with distilled water and then with acetone. It was then dried *in vacuo* (~130 torr) at 60°C.

CARBANILATION

For the hydrolyzed α -pulp and Avicel, 0.2 g of air-dried cellulose was placed in a 100 mL round bottomed flask together with a stirring bar. The flask and contents were then dried overnight *in vacuo* (~130 torr) at 60°C.

Approximately 50 mL of anhydrous pyridine was added to the flask which was then immersed in an oil bath maintained at 80°C. While the suspension was stirred, 4 mL of phenyl isocyanate was added. The flask was then sealed with a Teflon stopper.

Reaction proceeded in a well-stirred solution for 48 h, at which time the clear yellow solution was removed from the oil bath and 4 mL of methanol added to react with the excess phenyl isocyanate. The reaction time (48 h) and temperature (80°C) utilized are those recommended by Schroeder and Haigh¹⁰ to prevent depolymerization of the cellulose during the reaction.

When the above carbanilation procedure was used on the α -pulp, it was observed that after 2 days the reaction mixture contained undissolved cellulose. Sundquist and Rantanen¹ have noted similar difficulties in carbanilating regenerated cellulose. They found that such samples could be derivatized if they were first conditioned by soaking in water and then subjected to solvent exchange with pyridine. When the α -pulp was preconditioned by this method, most of the cellulose appeared to go into solution; however, small amounts of solid material still remained after 2 days of reaction.

SAMPLE PREPARATION

Three different methods were used to prepare samples for SEC analysis: (1) the CTC was precipitated in methanol; (2) the CTC was precipitated in a methanol/water mixture; and (3) the pyridine was evaporated from the

reaction mixture, thereby producing a sample containing all of the nonvolatile products of the derivatization procedure.

Precipitation in Methanol. Five milliliters of the pyridine reaction mixture was added dropwise to 100 mL of methanol which was cooled with an external dry ice bath. (In cold methanol, the precipitates from the Avicel and hydrolyzed α -pulp samples consisted of larger aggregates than the precipitates formed in methanol at room temperature.) The solution was then warmed to room temperature and centrifuged to separate the precipitated products. The clear supernatant was decanted and filtered through a medium porosity glass filter to remove any entrained solids. The precipitate was transferred to a medium porosity glass filter and washed with methanol.

The methanol was removed from the supernatant by evaporation at 40°C. The resulting syrupy, yellowish liquid and the precipitated solids were each dissolved in approximately 15 mL of acetone. Two milliliter aliquots of the acetone solutions were transferred to 10 mL vials and the acetone was evaporated with a stream of nitrogen. The residual material was dried overnight *in vacuo* at 60°C to remove any traces of pyridine and then redissolved in 10 mL of tetrahydrofuran (THF). The THF solutions were used as stock solutions for the SEC analysis.

Precipitation in Methanol/Water. The procedure was the same as that for precipitation in methanol except a 50/50 (v/v) mixture of methanol and water was used to precipitate and wash the recovered solids.

Evaporation of the Reaction Mixture. Five milliliters of the pyridine reaction mixture was transferred to a 50 mL round bottomed flask and the pyridine evaporated *in vacuo* (~ 20 torr) at 40°C. The syrupy liquid which remained was dissolved in approximately 15 mL of acetone. A 2 mL aliquot of this solution was prepared for SEC analysis as described above. The sample prepared by this method represented the contents of the entire reaction mixture.

SIZE EXCLUSION CHROMATOGRAPHY (SEC)

Samples from the THF stock solutions were diluted and filtered through a 0.45 μm filter prior to analysis. The resultant polymer concentrations were less than 0.01%, a level which should minimize concentration effects on the SEC analysis.¹²

The CTC samples were analyzed on a Spectra-Physics SP8100 liquid chromatograph using Shodex KF803 and KF805 SEC columns connected in series. A flow rate of 1 mL/min was used for the THF eluent. The CTC in the eluent was detected using a UV spectrophotometer (Spectra-Physics SP8400) operated at 235 nm. The signal from the UV detector was fed to an Apple IIe computer for data storage and calculation of molecular weight averages.

The correlation of molecular weight with retention volume for the CTC samples was obtained using the universal calibration procedure based on narrow MWD polystyrene standards. The Mark-Houwink coefficients for CTC in THF used in the present analysis were those reported by Danhelka et al.⁸ ($K = 0.0053$, $a = 0.84$). The coefficients used for polystyrene were

an average of those reported by Kolinsky and Janca¹³ ($K = 0.0112$, $\alpha = 0.72$).

RESULTS AND DISCUSSION

The chromatograms of the various CTC samples are shown in Figures 1–6. CTC was not detected in the methanol/water supernatant; thus, chromatograms for these samples are not presented. A linear regression on the region of each chromatogram between retention volumes B1 and B2 was used to define the baseline. The beginning and end of the CTC peak were taken at retention volumes P1 and P2, respectively. The large peak eluting after a retention volume of 22 mL is due to the reaction byproducts (*N,N'*-diphenyl urea and methyl phenylcarbamate). The number and weight average degrees of polymerization (monomer molecular weight = 519) calculated from the baseline corrected chromatograms are given in Table I. The high molecular weight shoulder in Figure 6(b) was attributed to pre-

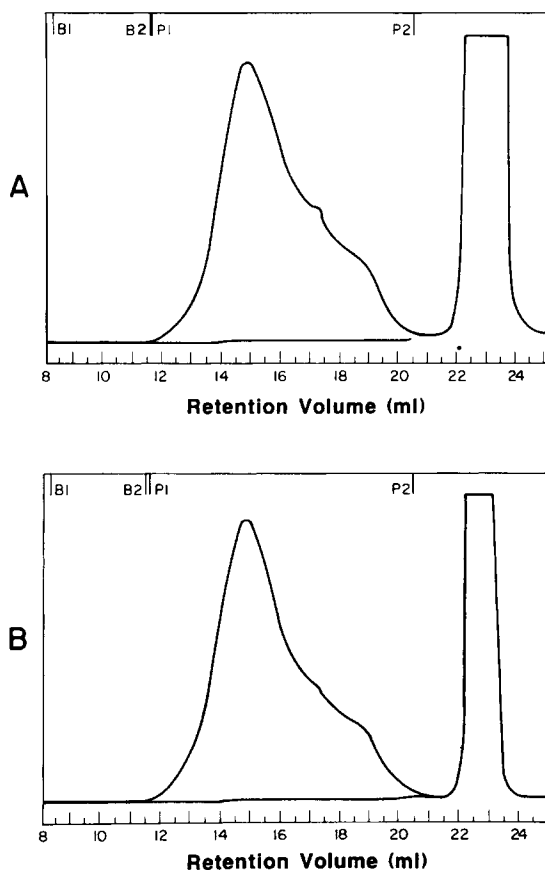


Fig. 1. Chromatograms of CTC derived from Avicel prepared by (A) evaporation of the reaction mixture ($DP_w = 197$; $DP_n = 46$) and (B) precipitation in methanol/water ($DP_w = 216$; $DP_n = 51$).

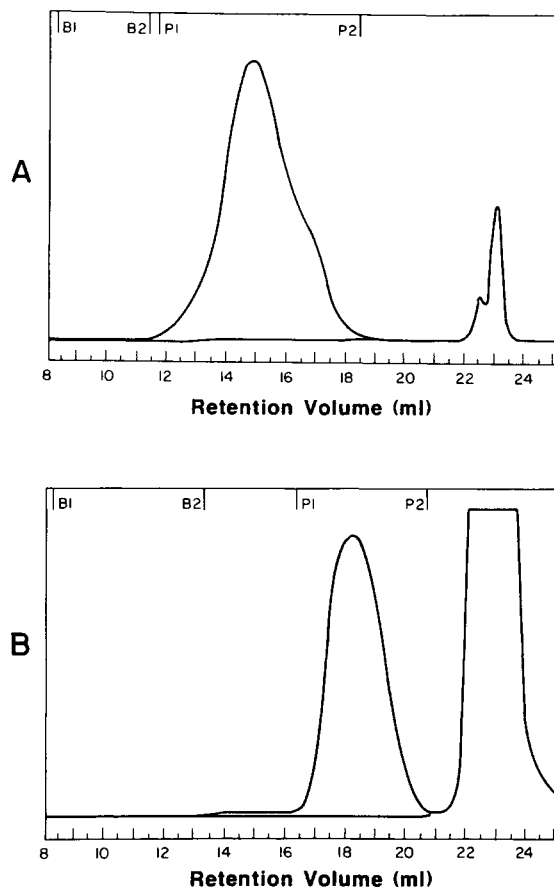


Fig. 2. Chromatograms of the fractions of CTC derived from Avicel which were (A) precipitated in methanol ($DP_w = 267$; $DP_n = 125$) and (B) soluble in methanol ($DP_w = 18$; $DP_n = 13$).

TABLE I
Number Average Degrees of Polymerization (DP_n) and Weight Average Degrees of Polymerization (DP_w) for the Samples Shown in Figures 1-6

Sample	DP_n	DP_w
Avicel—evaporated	46	197
Avicel—MeOH/water precipitate	51	216
Avicel—MeOH precipitate	125	267
Avicel—MeOH supernatant	13	18
Hydrolyzed α -pulp—evaporated	29	102
Hydrolyzed α -pulp—MeOH/water precipitate	32	110
Hydrolyzed α -pulp—MeOH precipitate	64	133
Hydrolyzed α -pulp—MeOH supernatant	12	16
α -pulp—evaporated	100	708
α -pulp—MeOH/water precipitate	104	765
α -pulp—MeOH precipitate	211	882
α -pulp—MeOH supernatant	13	20

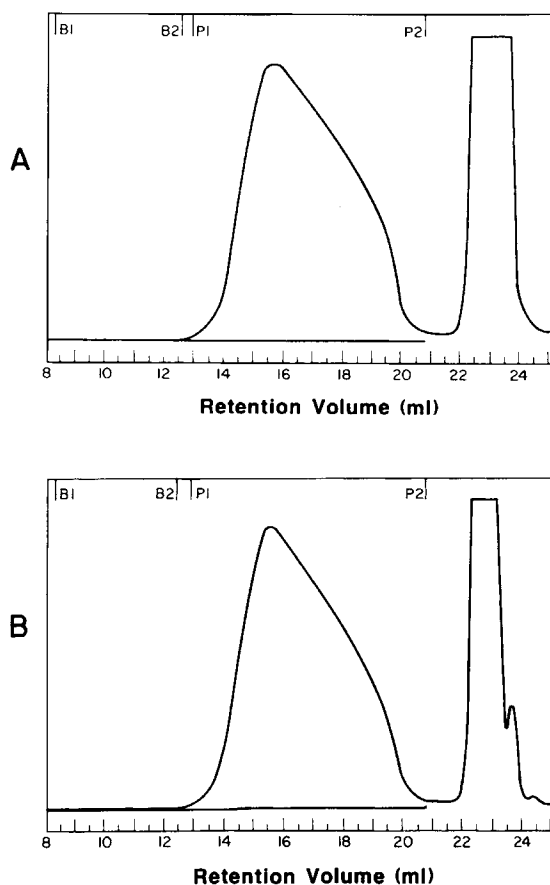


Fig. 3. Chromatograms of CTC derived from hydrolyzed α -pulp prepared by (A) evaporation of the reaction mixture ($DP_w = 102$; $DP_n = 29$) and (B) precipitation in methanol/water [$DP_w = 110$; $DP_n = 32$].

cipitated solids not removed by filtration of the supernatant. This material was not included in calculating the average degrees of polymerization of this sample.

From Figures 2, 4, and 6, it is apparent that the methanol precipitation procedure results in fractionation of all of the CTC samples. The chromatograms of the CTC which was soluble in methanol indicate that CTC polymer eluting with a retention volume greater than approximately 17 mL is fractionated by precipitation in methanol. Based on the universal calibration technique, this indicates that CTC molecules with degrees of polymerization less than approximately 40 cannot be completely recovered by precipitation in methanol. Although the DP of the CTC polymers characterized by a retention volume of 17 mL may be overestimated by using the universal calibration procedure in the low molecular weight range,⁴ all of the samples of cellulose studied contained a fraction of low molecular weight material which was not recovered by precipitation.

The chromatogram of the CTC which was soluble in methanol and the chromatogram of the CTC which was precipitated in methanol represent

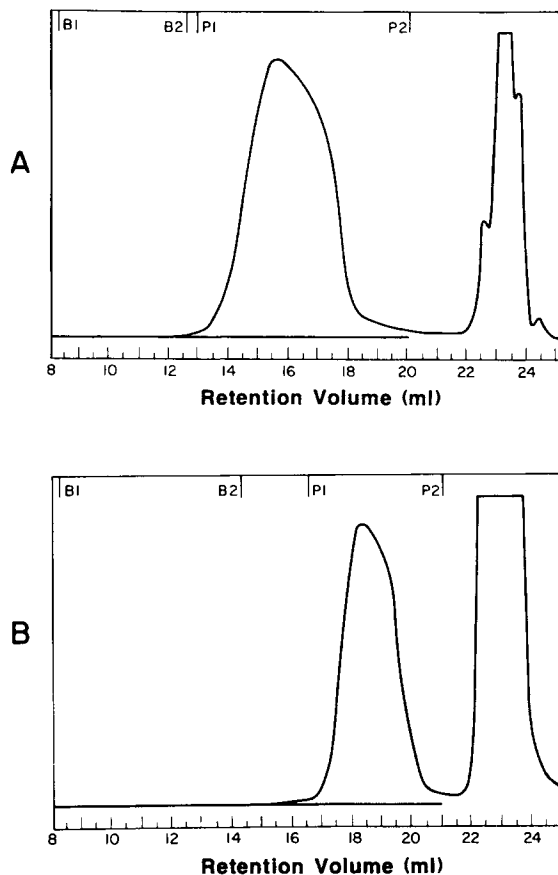


Fig. 4. Chromatograms of the fractions of CTC derived from hydrolyzed α -pulp which were (A) precipitated in methanol ($DP_w = 133$; $DP_n = 64$) and (B) soluble in methanol ($DP_w = 16$; $DP_n = 12$).

all of the CTC in the original reaction mixture. Therefore, it should be possible to generate the chromatogram of the sample obtained by evaporating the pyridine by taking a linear combination of the chromatograms of the samples which were precipitated and soluble in methanol. The percentage of the total area contributed by the chromatogram of the soluble fraction is the weight fraction of the original sample not precipitated in methanol.

For example, Figure 7 shows the linear combination of the baseline-corrected chromatograms in Figures 4(a) and 4(b) weighted such that the soluble fraction contributes 26% of the total area. The similarity of Figures 7 and 3(a) indicates that approximately 26% of the CTC prepared from hydrolyzed α -pulp was not precipitated in methanol. By a similar approach it was determined that approximately 20% of the weight of the CTC derived from Avicel was soluble in methanol while approximately 5% of the CTC derived from α -pulp was soluble.

The disadvantage of recovering CTC derived from Avicel and from hydrolyzed α -pulp by precipitation in methanol is thus apparent. For the α -

pulp sample, even though only 5% of the CTC was not recovered, this fraction had a large influence on the number average degree of polymerization determined for the sample. Sundquist and Rantanen¹ have pointed out that the major use of CTC derivatives in the near future will be to characterize dissolving pulps which are used as feedstocks for the production of cellulose derivatives.¹⁴ Since the end-use properties of these derivatives could be markedly influenced by the presence of a low molecular weight fraction, it is important to recognize that the precipitate recovered in methanol may not represent the original MWD of the cellulose.

The degrees of polymerization of the samples precipitated in the methanol/water mixture are in closer agreement with the values obtained for the evaporated samples; however, they are all 4–10% higher. This fact indicates that precipitation even with this more polar mixture leads to some fractionation of CTC. In addition, comparison of the byproduct peaks in Figures 1(a), 1(b), and 2(a) shows that little separation of the CTC from the reaction byproducts is achieved in the methanol/water mixture.

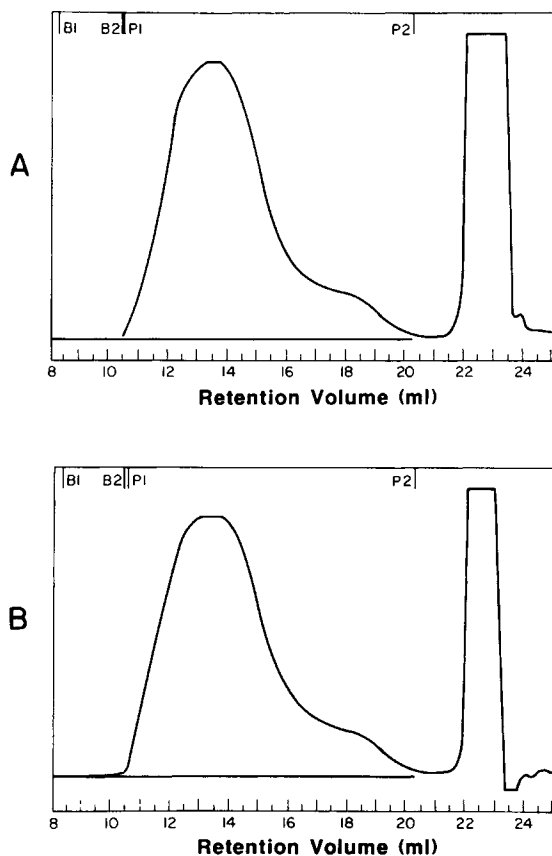


Fig. 5. Chromatograms of CTC derived from α -pulp prepared by (A) evaporation of the reaction mixture ($DP_w = 708$; $DP_n = 100$) and (B) precipitation in methanol/water ($DP_w = 765$; $DP_n = 104$).

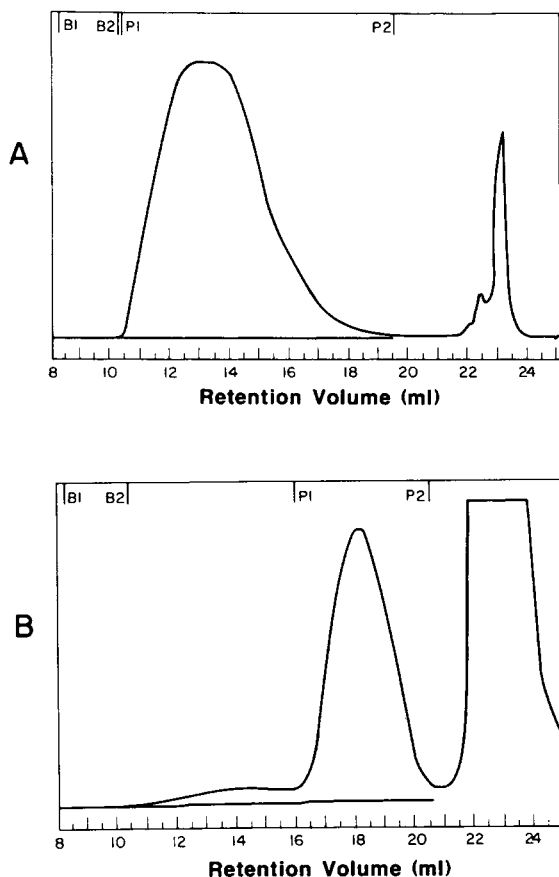


Fig. 6. Chromatograms of the fractions of CTC derived from α -pulp which were (A) precipitated in methanol ($DP_w = 882$; $DP_n = 211$) and (B) soluble in methanol ($DP_w = 20$; $DP_n = 13$).

It should be pointed out that precipitation of CTC samples in ethanol³ should also lead to fractionation since ethanol is a less polar solvent than methanol. In addition, washing precipitated CTC samples with methanol¹⁵ or ethanol would result in the loss of any low molecular weight CTC.

CONCLUSIONS

Precipitation of cellulose tricarbaniolate in methanol will fractionate CTC if the original cellulose contains material with DP less than approximately 40. The weight fraction of CTC lost by precipitation in methanol was appreciable for samples prepared from hydrolyzed α -pulp and Avicel (26% and 20%, respectively). Although only 5% of the CTC from α -pulp was not precipitated in methanol, this fraction had a large influence on the number average molecular weight of the sample. Precipitation in a methanol/water mixture resulted in less fractionation; however, since the reaction byproducts are also precipitated in this case, the use of the methanol/water mixture

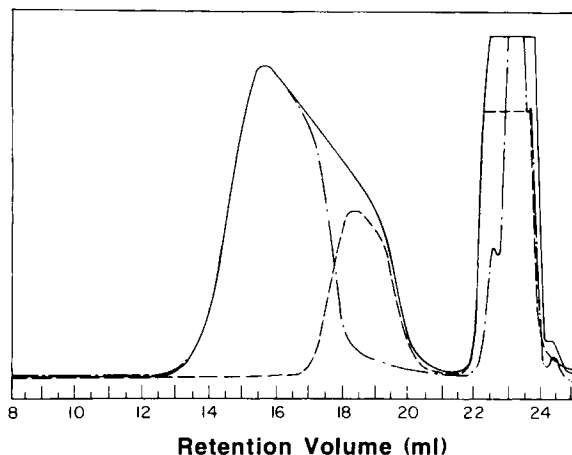


Fig. 7. Linear combination of the chromatograms of the methanol precipitated and methanol soluble fractions of the CTC derived from hydrolyzed α -pulp. The soluble fraction contributes 26% of the total area of the linear combination.

offers no advantage over the simpler method of analyzing all of the non-volatile products from the derivatization reaction. These results indicate that when the carbanilate derivative of cellulose is used to characterize the MWD of cellulose by SEC, care must be taken to ensure that the CTC is not fractionated during preparation for analysis. SEC analysis of the non-volatile products from the derivatization reaction offers a useful method for determining if the original cellulose contains a low molecular weight fraction.

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