Surface Chlorination of Polypropylene Film by CHCl₃ Plasma

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SYNOPSIS

Polypropylene films were treated with the $CHCl_3$ plasma, and their chemical composition was analyzed with XPS and ART IR spectroscopy. The $CHCl_3$ plasma irradiation made polypropylene films hydrophilic. The advancing contact angle decreases from 95° for the untreated to about 73° for the $CHCl_3$ plasma-treated films. In the $CHCl_3$ plasma irradiation, the chlorination occurs, and $C-Cl$, $C-Cl_2$, and $C-Cl_3$ units are formed in the polypropylene films. Simultaneously with the chlorination, unsaturated units ($C=C$ and conjugated $C=C$ units) are formed from dehydrogen chlorination of the chlorinated products, but the oxygen incorporation into the films is low. The $CHCl_3$ plasma is preferred in chlorination of polypropylene films to the CCl_4 plasma. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene film has distinguished properties such as clearness, toughness, is light in weight, relatively high temperature resistant, low-priced, and widely used as a raw material for package. The film, however, is difficult to adhere directly to other materials because of a hydrophobic surface. An effective manner to improve the adhesion is hydrophilic modification. Typical methods are primer treatment, surface chlorination by chlorine compounds, surface oxidation by corona discharge, or plasma treatment.[1-16]

Plasma treatment is a distinguished surface modification process, and the depth modified by the treatment is restricted to a few hundreds angstroms from the topmost layer of the film surface. Therefore, the plasma treatment never injures bulk properties such as toughness, crystallinity, thermal stability, etc. This is an advantage of the plasma treatment, especially for the surface modification of organic thin films.

Chlorine moieties as well as oxygen moieties such as OH, $C=O$, and $C(O)OR$ groups could be ex-

pected to contribute to an increase in hydrophilicity of the film surfaces. For example, the surface energy of polyvinyl chloride and polyvinylidene chloride is 41.5 and 39.9 mJ/m^2, respectively, and that of polyethylene and polypropylene is 33.2 and 29.6 mJ/m^2, respectively.[17] Chlorinated polypropylene is also a good adhesive for polypropylene materials.[18] From the standpoint of adhesion improvement, surface chlorination of polypropylene films is of interest. Polypropylene, popularly, is chlorinated with chlorine in a suspension of aqueous or organic solvents such as carbon tetrachloride in the presence of free-radical initiators. The chlorination reaction of polyolefins is free radical in nature. A chlorine radical abstracts hydrogen from the hydrocarbon chain to form a carbon radical in the chains. The carbon radical, furthermore, reacts with chlorine to yield a chlorinated product and a new chlorine radical. This process is a chain reaction.[19,20] This reaction mechanism predicts that plasma could be preferred in the chlorination of polypropylene because plasma contains many radical species. This investigation concerns surface modification of polypropylene film by chlorination using the plasma treatment. The $CHCl_3$ plasma was used as a chlorination reagent, and the chemical composition of the plasma-treated surfaces was investigated with the contact angle method, XPS, and ATR IR spectroscopy.

EXPERIMENTAL

Materials

Polypropylene film used for the plasma treatment was kindly provided from Idemitsu Petrochemical Co. and received in a 215-mm wide and 25-μm thick form. The polypropylene film was cut to a size of 50 $\times$ 10 mm, and provided for the plasma chlorination experiment. Chloroform used as a reagent for the plasma chlorination was analytical grade (Tokyo Kasei Co.) and used without further purification.

Plasma Treatment

A home-made plasma reactor, which was a capacitively coupled system at a 20 kHz frequency, was used for the plasma treatment. The reactor consisted of a bell jar (400-mm diameter, 470-mm height) with a monomer inlet, a pair of parallel stainless steel electrodes (150 $\times$ 150 mm), a substrate stage, a pressure gauge, and a vacuum system consisting of a rotary and a diffusion pump. A schema of the reactor was presented in a previous paper.[21] The polypropylene film was mounted on the sample stage, and was placed midway between the stainless steel electrodes that were at a space of 100 mm.

The experimental procedures for the plasma treatment of the polypropylene films were essentially the same as reported elsewhere.[21] The reactor was evacuated to approximately 0.13 Pa, and then the vapor of $CHCl_3$ was introduced into the reaction chamber at a flow rate of 10 cm^3 (STP)/min adjusted by a metering valve. The plasma treatment was performed at a given discharge current of 50 to 150 mA at a 20-kHz frequency at a system pressure of 13.3 Pa for a given duration of 1–15 min.

Advancing Contact Angle of Water and Surface Energy

The advancing contact angles of water, glycerol, formamide, diiodomethane, and tricresyl phosphate on the plasma-treated polypropylene film surfaces were measured at 20°C using an Erma contact angle meter with a goniometer, model G-1. The advancing contact angle of the liquids (1 μL) was determined from an average of 10 specimens. The surface energy of the plasma-treated polypropylene film was estimated from the data of the advancing contact angles against the five liquids according to Kaelble's method.[22]

Infrared and X-Ray Photoelectron Spectra

The ATR IR spectra for the plasma-treated polypropylene film were recorded on a Horiba Fourier transform spectrometer FT 300 with a MTC detector. The crystal of KRS-5 was used for the ATR measurement, and the incidence angle of infrared light was 45°. The penetration depth of IR light in the ranges of 3000–400 cm^{-1} is estimated to be about 0.66–5.0 μm. The spectral resolution was 0.5 cm^{-1}, and 100–200 scans were recorded on each sample.

The XPS spectra for the plasma-treated polypropylene films were obtained on an Ulvac-Phi spectrometer 5400 using an nonmonochromatic MgK_α photon source. The anode voltage was 15 kV, the wattage 400 W, and the background pressure in the analytical chamber 1 $\times$ 10^{-7} Pa. The analysis area of the film specimen was 1.1-mm diameter. The take-off angle of the analyzer against the face of the film specimen was 45°. The C_{1s} and Cl_{2p} spectra were decomposed by fitting Gaussian functions to an experimental curve using a nonlinear, least-squares curve-fitting program supplied by Ulvac–Phi. The decomposed C_{1s} component appearing at the lowest binding energy scale was corrected at 285.0 eV to eliminate charging effects. The sensitivity factors (S) for core levels were $S(C_{1s})$ = 0.296, $S(Cl_{2p})$ = 0.891, and $S(O_{1s})$ = 0.711.

RESULTS AND DISCUSSION

Advancing Contact Angle of $CHCl_3$ Plasma-Treated Polypropylene Films

The $CHCl_3$ plasma irradiation made the polypropylene films hydrophilic. Figure 1 shows the advancing contact angle of water against the plasma-treated polypropylene surface as functions of the plasma irradiation time and the plasma discharge current. The advancing contact angle of water against the plasma-treated polypropylene films, as shown in Figure 1, decreased with increasing the plasma irradiation time, went to a minimum, and then, increased as the plasma irradiation time increased. Such changes in contact angle by varying the plasma irradiation time are observed for all the plasma-treated polypropylene films independently of the plasma discharge current. A minimum of the advancing contact angle is about 73° for all the plasma-treated polypropylene, and the irradiation time required for reaching the minimum of the contact angle depends on the magnitude of discharge current: 11, 9, and 3 min at discharge currents of
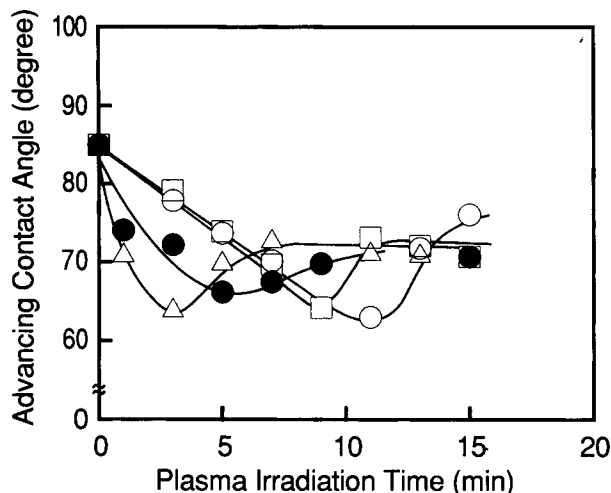
Figure 1 Advancing contact angle of water against plasma-treated polypropylene film surface as a function of plasma irradiation time; (○) treated with CHCl₃ plasma at a discharge current of 50 mA; (□) treated with CHCl₃ plasma at 100 mA; (△) treated with CHCl₃ plasma at 150 mA; (●) treated with CCl₄ plasma at 50 mA.

50, 100, and 150 mA, respectively. These advancing contact angle changes implies:

1. The surface modification reactions with the CHCl₃ plasma proceed mainly in two stages. During shot irradiation time within 3–11 min, hydrophilic modification is predominant, and at longer irradiation time more than 11 min, hydrophobic rather than hydrophilic modification occurs.
2. A high plasma discharge current leads to quick accomplishment of hydrophilic modification.
3. Hydrophilicity accomplished by the CHCl₃ plasma (a minimum contact angle) is independent of the plasma discharge current, and a minimum contact angle is about 73°.

Hydrophilicity produced by the CHCl₃ plasma irradiation is compared with that by the CCl₄ plasma, which was reported in a previous article. The CCl₄ plasma effect is duplicated in Figure 1. The two plasma irradiation experiments were carried out using the same plasma reactor and under the same irradiation conditions, a discharge current of 50 mA, a reaction pressure of 13.3 Pa, and a plasma gas flow rate of 10 cm³/min, except for the plasma gases, CHCl₃ and CCl₄. The CCl₄ plasma irradiation also showed similar changes in advancing contact angle to the CHCl₃ plasma irradiation: The advancing

contact angle of water decreased as the plasma irradiation time increased up to 5 min, and afterward, increased with increasing the plasma irradiation time. The CHCl₃ plasma irradiation was slightly effective in hydrophilic modification compared with the CCl₄ plasma irradiation because a minimum contact angle is 73° and 76° for the CHCl₃ plasma (at an irradiation of 11 min) and the CCl₄ plasma (5 min irradiation), respectively, which corresponded to a surface energy of about 35.5 and 33.0 mJ/m². These surface energies are larger than that of polypropylene, 29.6 mJ/m², but are smaller than that of polyvinyl chloride, 41.5 mJ/m². The Parachor concept concerns the contribution of chlorine substitution in polypropylene to surface energy.[23] The surface energy, γ_s, is estimated from eq. (1), where P_i and V_i are the contribution of structural and atomic groups to Parachor parameter and molar volume, respectively.

$$\gamma_s = \left(\frac{\sum P_i}{\sum V_i}\right)^4. \tag{1}$$

The estimation from eq. (1) implies that the chlorine substitution at the primary carbon atom was the most effective to increase the surface energy, and that the chlorine substitution at the tertiary carbon atom was ineffective. The surface energy is estimated to be 40.7 mJ/m² for polypropylene substituted with chlorine at the primary carbon,

$$\left(\begin{array}{c} CH_2Cl \\ | \\ -CH_2-CH- \end{array}\right)_n ;$$
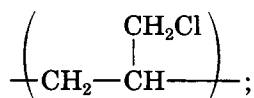
36.6 mJ/m² for polypropylene chlorine-substituted

$$\text{at the secondary carbon,} \left(\begin{array}{c} CH_3 \\ | \\ -CHCl-CH- \end{array}\right)_n ; \text{ and}$$

33.2 mJ/m² for polypropylene chlorine-substituted

$$\text{at the tertiary carbon,} \left(\begin{array}{c} CH_3 \\ | \\ -CH_2-CCl- \end{array}\right)_n . \text{ The}$$

comparison in surface energy between the experimental and the estimation from the Parachor concept suggests that a main of the chlorine substitution in polypropylene occurring in the CHCl₃ plasma may be at tertiary carbon. The chlorine substitution reaction will be discussed in a later section.

Chemical Composition of Plasma-Treated Polypropylene

The atomic composition for the plasma-treated polypropylene surface was analyzed by XPS to in-

vestigate what reaction had occurred in the $CHCl_3$ plasma irradiation. Two levels of the $CHCl_3$ plasma irradiation times at a constant discharge current were selected to prepare specimens for the XPS measurement: The levels of the $CHCl_3$ plasma irradiation times at a constant discharge current of 50 mA are 5 and 15 min, 5 and 11 min at 100 mA, and 1 and 7 min at 150 mA. A pair of the irradiation times at each discharge current corresponded to the irradiation conditions before and after the irradiation time when the advancing contact angle reached a minimum in the advancing contact angle curve versus the irradiation time (Fig. 1). Table I, which contains analytical results for the specimens, shows that all the $CHCl_3$ plasma-treated polypropylene films possess a large amount of chlorine and a small amount of oxygen. The Cl/C atomic ratio is 0.34–0.91 and is about 7–10 times larger than the O/C atomic ratio (0.05–0.09). This indicated that chlorination reactions occurred in the $CHCl_3$ plasma irradiation. Effects of the $CHCl_3$ plasma irradiation was a contrast in atomic composition to those of the CCl_4 plasma irradiation reported in previously.[21] The CCl_4 plasma irradiation leads to the incorporation of oxygen as well as chlorine into the polypropylene film surface (Table I). For the CCl_4 plasma-treated polypropylene films, the Cl/C and O/C atomic ratios were 0.37 and 0.26 at a discharge current of 50 mA, and were 0.13 and 0.50 at 150 mA, respectively. High oxygen concentration in the CCl_4 plasma-treated polypropylene films may be due to products from etching reactions of activated chlorine atoms at the electrode surface. The etching reactions occurred in the CCl_4 plasma as discussed in a previous

study.[21] From comparison of the atomic composition, we concluded that the $CHCl_3$ plasma irradiation is preferred in the chlorination to the CCl_4 plasma irradiation.

The Cl_{2p} core level spectra for the polypropylene films treated with $CHCl_3$ plasma at a discharge current of 50 mA for 15 min and at 150 mA for 7 min (although these spectra are not represented here for the sake of brevity) were decomposed into two components whose peaks positioned at 202.4 and 204.0 eV. The components were not ionic but nonionic, and were assigned to $Cl_{2p3/2}$ and $Cl_{2p1/2}$ in Cl—C bonds. If an ionic Cl component was contained, the ionic Cl will be observed at lower binding energy (at 198–199 eV for $Cl_{2p3/2}$ and at 200–201 eV for $Cl_{2p1/2}$).[24] From the spectral result, we concluded that all the chlorine incorporated into the polypropylene film surface by the $CHCl_3$ plasma was nonionic and Cl—C type bonds. This conclusion indicated that no sputter etching reaction occurred at the electrode surfaces in the $CHCl_3$ plasma.

The C_{1s} spectra for the $CHCl_3$ plasma-treated films were decomposed into four components whose peak appeared at 285.0, 286.4–286.8, 288.6–288.9, and 289.2–290.0 eV, which were assigned to CH, C—Cl and C—O, C—Cl_2, and C—Cl_3, respectively.[25] The peak 2, C—Cl and C—O components, could not be separated because the chemical shift for the two components was almost the same in magnitude (1.56 eV for the C—Cl component and 1.46–1.51 eV for the C—O component).[25] Therefore, we concluded that the peak 2 appearing at 286.4–286.8 eV is tentatively assigned as a mixture of C—Cl and C—O components. Because the

Table I   Chemical Composition of Plasma-Treated Polypropylene Film Surface

	Plasma Treatment Conditions		Atomic Composition		C1s Spectra (Relative Peak Area, %)					
Plasma	Discharge Current (mA)	Irradiation Time (min)	Cl/C Atomic Ratio	O/C Atomic Ratio	Peak 1 CH	Peak 2 C—Cl C—O	Peak 3 C—Cl_2	Peak 4 C—Cl_3	Peak 3' C=O	Peak 4' C(O)O
No			< 0.01	0.02	96	4				
$CHCl_3$	50	5	0.55	0.08	25	50	21	4		
	50	15	0.91	0.05	19	44	26	11		
	100	5	0.64	0.07	24	50	12	14		
	100	11	0.61	0.07	24	49	19	18		
	150	1	0.65	0.06	21	50	21	8		
	150	7	0.34	0.09	26	48	22	4		
CCl_4	50	5	0.37	0.27	48	32			12	8
	150	7	0.13	0.50	77	10			6	7

chlorine concentration at the $CHCl_3$ plasma-treated film surfaces was higher than the oxygen concentration, a great part of peak 2 may be attributable to the C — Cl component. Typical C_{1s} spectra are shown in Figure 2. The relative concentration of the C_{1s} components for the $CHCl_3$ plasma-treated polypropylene films is listed in Table I as a function of the plasma treatment conditions. There was no remarkable difference in the distribution of C_{1s} components between the six $CHCl_3$ plasma-treated films, although the films were plasma treated under different conditions: the peak 2 (the C — Cl and C — O component) was a main component of the C_{1s} features, and its relative concentration accounted for about 50% of the total carbons existing within the sampling depth of photoelectrons. The peak 1 and 3 (CH and C — Cl_2 components) were about 19–26% and the peak 4 (the C — Cl_3 component) was as small as 4–18% of the total carbons. These C_{1s} spectra for the $CHCl_3$ plasma-treated film surfaces were different from those for the CCl_4 plasma-
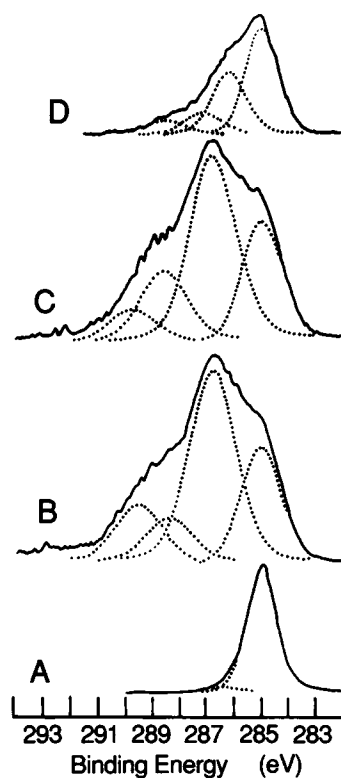
Figure 2 XPS (C_{1s}) spectra for plasma-treated polypropylene films: (A) untreated; (B) treated with $CHCl_3$ plasma at a discharge current of 100 mA for 5 min; (C) treated with $CHCl_3$ plasma at a discharge current of 100 mA for 11 min; (D) treated with CCl_4 plasma at a discharge current of 100 mA for 5 min.
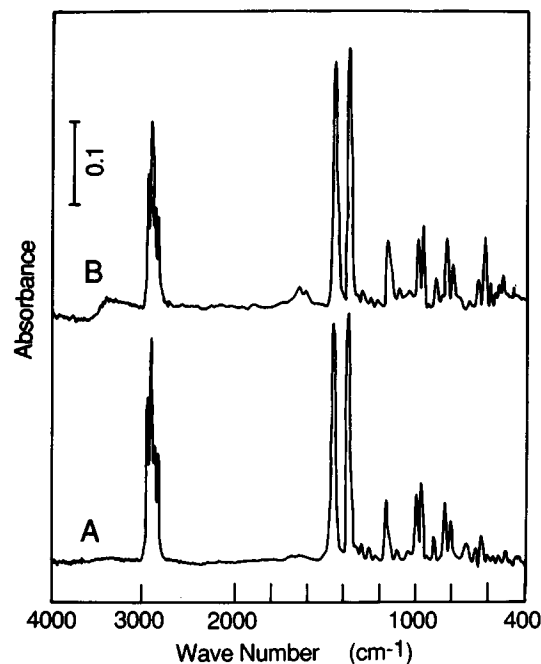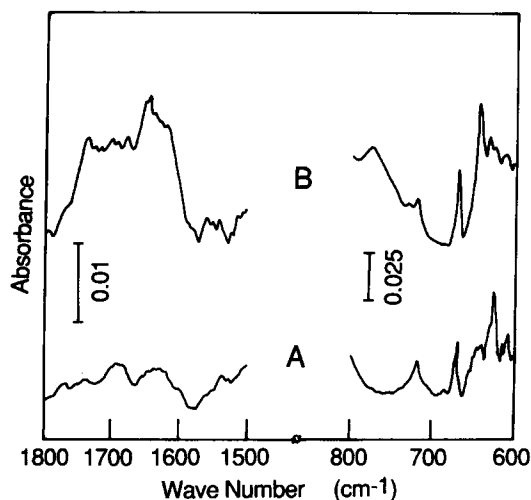

Figure 3 ATR IR spectra for $CHCl_3$ plasma-treated polypropylene: (A) untreated; (B) treated with $CHCl_3$ plasma for 5 min.

treated ones. To compare the two spectra, a typical C_{1s} spectrum for the CCl_4 plasma-treated film at 50 mA is illustrated in Figure 2. The C_{1s} spectrum for the CCl_4 plasma-treated film was decomposed into four components of which the peak appeared at 285.0 (CH), 286.5 (C — Cl and C — O), 287.4 (C=O), and 288.9 [C(O)O].[25] Comparison of the C_{1s} spectra showed that the CCl_4 plasma-treated film surface possessed the C — Cl component but no C — Cl_2 and C — Cl_3 components. On the other hand, the $CHCl_3$ plasma-treated film surfaces possess C — Cl_2 and C — Cl_3 components as well as a C — Cl component. This was a striking difference between the $CHCl_3$ plasma-treated and CCl_4 plasma-treated films. The chlorination of polypropylene proceeded radically. In the early stages of reactions, the chlorination occurred probably at the tertiary carbon rather than at the primary and secondary carbons. As a result, C — Cl groups will be formed predominantly. After the early stage, the formation of C — Cl_2 and C — Cl_3 groups will be preferred because a chlorine effect accelerated chlorination on the chlorinated carbons rather than not chlorinated carbons. At last, the C — Cl_2 and C — Cl_3 groups will increase relative to the C — Cl group.[19] Taking these reaction mechanisms into account, the $CHCl_3$ plasma is preferred in chlorination to the CCl_4 plasma, and highly chlo-

rine-substituted products could be obtained from the $CHCl_3$ plasma.

ATR IR spectra showed other information on reactions occurring at the interface between polypropylene film and the $CHCl_3$ plasma. Figure 3 shows typical ATR IR spectra for the $CHCl_3$ plasma-treated and the untreated polypropylene films. Although the $CHCl_3$ plasma-treated film shows strong absorption peaks at 2950, 2914, 2870, 2837, 1456, 1357, 1164, 997, 840, and 808 cm^{-1}, which are characteristic absorptions due to CH_3, CH_2, and CH stretching and deformation vibrations,[26] there are differences in the ranges of 1800–1600 cm^{-1} and 800–600 cm^{-1} between the $CHCl_3$ plasma-treated and the untreated film. Figure 4 shows expanded spectra in the ranges of 1800–1600 cm^{-1} and 800–700 cm^{-1}. In the 1800–1600 cm^{-1}, there are many absorption peaks at 1737 and 1718 cm^{-1} (C$=$O), 1701 cm^{-1} (—C(O)—CH$=$CH—), 1680 and 1652 cm^{-1} (C$=$C), and 1646 and 1620 cm^{-1} (conjugated C$=$C). In the 800–600 cm^{-1}, absorption peaks appear at 778, 732, and 645 cm^{-1}, which are assigned to C—Cl stretching vibration.[27] The absorption peaks at 778 and 732 cm^{-1} may be due to C—Cl stretching vibration in C—Cl_2 and C—Cl_3 units, and the absorption peak at 645 cm^{-1} may be due to C—Cl stretching vibration in C—Cl units.

These IR spectra indicate that the $CHCl_3$ plasma can surely make chlorination of polypropylene films. Simultaneously with the chlorination, unsaturated units (C$=$C and conjugated C$=$C units) are formed in the interaction with the $CHCl_3$ plasma.

Figure 4   ATR IR spectra for $CHCl_3$ plasma-treated polypropylene: (A) untreated; (B) treated with $CHCl_3$ plasma for 5 min.

The formation of the unsaturated units is believed to be products of dehydrogen chlorination from chlorinated polypropylene.

CONCLUSIONS

The $CHCl_3$ plasma treatment of polypropylene film surfaces was investigated from the viewpoint of chemistry of chlorination. The $CHCl_3$ plasma has the capability to chlorinate polypropylene surfaces and to change the surface property from hydrophobic to hydrophilic. C—Cl, C—Cl_2, and C—Cl_3 units are formed in polypropylene by the interactions with the $CHCl_3$ plasma. Simultaneously with the chlorination, unsaturated units (C$=$C and conjugated C$=$C units) are formed from dehydrogen chlorination of the chlorinated polypropylene. The formation of oxygen functionalities such as C—O, C$=$O, and C(O)O groups is lower than the CCl_4 plasma. The $CHCl_3$ plasma is preferred in surface chlorination of polypropylene to the CCl_4 plasma.

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