

Synthesis and Corrosion Protection Performance of Polydiphenylamine

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ABSTRACT: In recent years, the conducting polymers are used in organic coatings as a replacement of chromate based pigments. The effectiveness of polydiphenylamine (PDPA) in the vinyl coating towards the corrosion protection of steel in acidic environment has been found out. The polymer PDPA was synthesized by chemical oxidation of diphenylamine by ammonium persulfate in hydrochloric acid medium. The polymer was characterized by FTIR and XRD. The corrosion protection performance of the PDPA

containing 0–5% in vinyl coating on steel in 0.1N HCl has been assessed by electrochemical impedance spectroscopy. Coatings containing more than 3% PDPA are found to offer excellent corrosion protection of steel in acid media due to redox property of PDPA. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1707–1711, 2007

Key words: polydiphenylamine; corrosion; coatings; EIS; steel

INTRODUCTION

During the last two decades, intrinsically electronic conducting polymers, such as polyaniline and polypyrrole, have been studied for their corrosion protection properties of metals. The reviews^{1–4} summarize the studies made by several investigators on the corrosion protection of metals by conducting polymers. Organic coatings containing polyaniline have been shown to offer protection of steel in acid, neutral, and alkaline media.^{5–13} The role of dopants, such as phosphonic acid, sulfonic acid, etc., has been studied with respect to corrosion protection properties of steel.^{14–18} Recent study made by authors¹⁹ have shown that polydiphenylamine (PDPA) is an efficient inhibitor for prevention of corrosion of iron in acid. Hence a study has been made on the corrosion protection of steel by vinyl coating containing PDPA. Earlier studies on PDPA are mainly concerned with its magnetic properties,²⁰ sensor applications²¹ and sorption properties with phenolic compounds.²² In this article, the synthesis and characteristics of PDPA and its anti corrosive properties for steel are presented.

EXPERIMENTAL

Preparation of PDPA pigment

1M of distilled diphenylamine was dissolved in 500 mL of 4M solution of hydrochloric acid. Precooled 1M solution of ammonium persulfate was added

drop wise to the precooled diphenylamine–acid mixture for about 1.5 h with constant stirring. The reaction was conducted at $5^{\circ}\text{C} \pm 1^{\circ}\text{C}$. After the addition, the stirring was continued for 2 h for ensuring complete polymerization. A dark green colored conducting PDPA thus formed was filtered and repeatedly washed with distilled water to remove excess acid content. The polymer was dried in oven at about 80°C for 2 h. The dried PDPA was fine grinded using mortar and then used as pigment.

Characterization of PDPA

The X-ray diffraction pattern of PDPA was taken with Analytical (Model PW3040/60) X-ray diffractometer, using Cu K α radiation in the 2θ range $5\text{--}75^{\circ}$ at the scan range of $0.0170^{\circ} 2\theta$ with continuous scan type with scan step time of 15.5056 s. The infrared spectra of the polymer pelletized with KBr in the region of $2000\text{--}500\text{ cm}^{-1}$ were recorded on NICOLET 380 FTIR spectrometer using at room temperature. The morphology of the polymer was analyzed at a magnification of 1k, using Hitachi (Model S3000 H) scanning electron microscope, by spreading the pigment over a copper block over which gold was sputtered.

Preparation of PDPA containing paint

The PDPA containing paint was prepared using vinyl resin ($M_w = 30,000$) with 0–5% PDPA. The characteristics of paint and coating are: touch dry-1 h; complete dry-2 h; volume solids-30–35%; thickness per coat $50 \pm 5\ \mu\text{m}$; pvc-1–5%.

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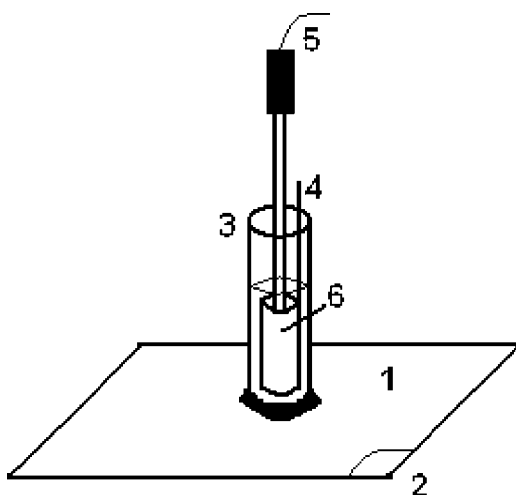


Figure 1 Experimental cell setup: (1) painted steel panel; (2) paint removed area for making working electrode contact; (3) glass tube; (4) platinum counter electrode; (5) SCE reference electrode; (6) test electrolyte.

Evaluation of corrosion resistant properties of the coating by EIS

Steel specimens of size $5 \times 5 \times 0.1 \text{ cm}^3$ were sand-blasted (SA 2.5) and degreased with trichloroethylene and coated with the developed paint. The total thickness of the coating was $100 \pm 5 \mu\text{m}$. A glass tube of 1.2 cm diameter of length 3 cm was fixed on the coated ms panel with adhesive (m seal) and the exposed area was 1.0 cm^2 to the solution. The solution of 3% NaCl was taken in the glass tube. A platinum foil and a saturated calomel electrode were placed inside the glass tube. The schematic diagram of the experimental cell assembly is shown in Figure 1. The assembly was connected to electrochemical impedance analyzer (PARSTAT 2273, EG, and G). Impedance measurements were carried out for a frequency range of 100 KHz–0.1 Hz with an a.c. amplitude of 20 mV for different immersion time up to 60 days. The impedance values are reproducible $\pm 2\text{--}3\%$. From the impedance plots, the coating resistance (R_c) and the coating capacitance (C_c) values were calculated using the equivalent circuit shown in Figure 2. In the equivalent circuit, R_s is the solution resistance, R_c is the coating resistance, and CPE is the constant phase element of the coating capacitance (C_c).

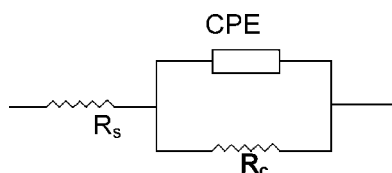


Figure 2 Equivalent circuit for painted steel panel.

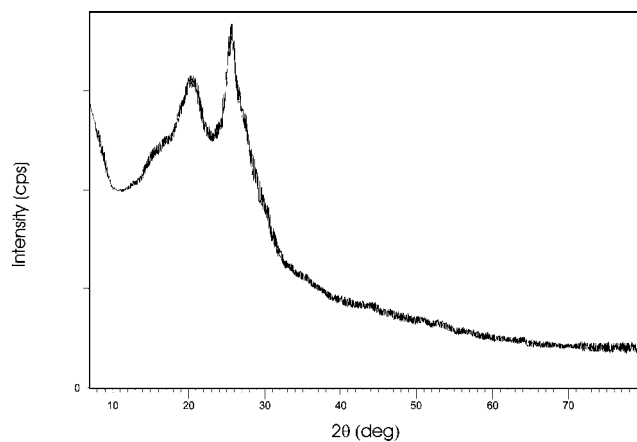


Figure 3 X-ray diffraction pattern of polydiphenylamine pigment.

Assumption of a simple $R_c\text{--}C_c$ is usually a poor approximation. For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used, which is defined in impedance representation as

$$Z(\text{CPE}) = Y_0^{-1}(j\omega)^{-n}$$

where Y_0 is the CPE constant, ω is the angular frequency (in rad s^{-1}), $j^2 = -1$ is the imaginary number and n is the CPE exponent. Depending on n , CPE can represent resistance [$Z(\text{CPE}) = R$, $n = 0$], capacitance [$Z(\text{CPE}) = C$, $n = 1$], inductance [$Z(\text{CPE}) = L$, $n = -1$], or Warburg impedance for ($n = 0.5$).²³ The following equation is used to convert Y_0 into C_c is,²⁴

$$C_c = Y_0(\omega_m'')^{n-1}$$

where C_c is the coating capacitance and ω_m'' is the angular frequency at which Z'' is maximum. The experiments were carried out for a period of 75 days.

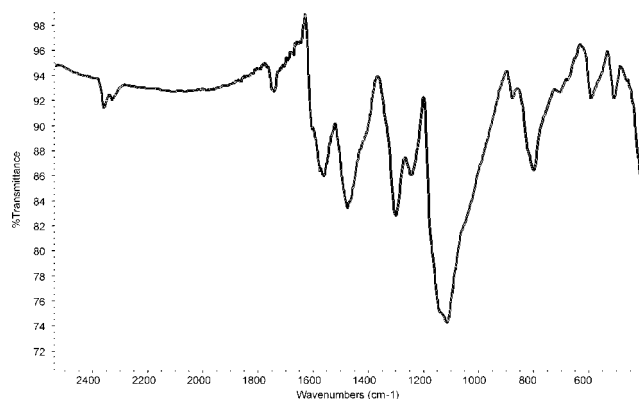
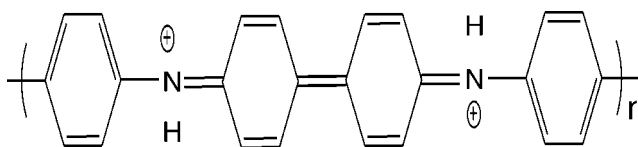
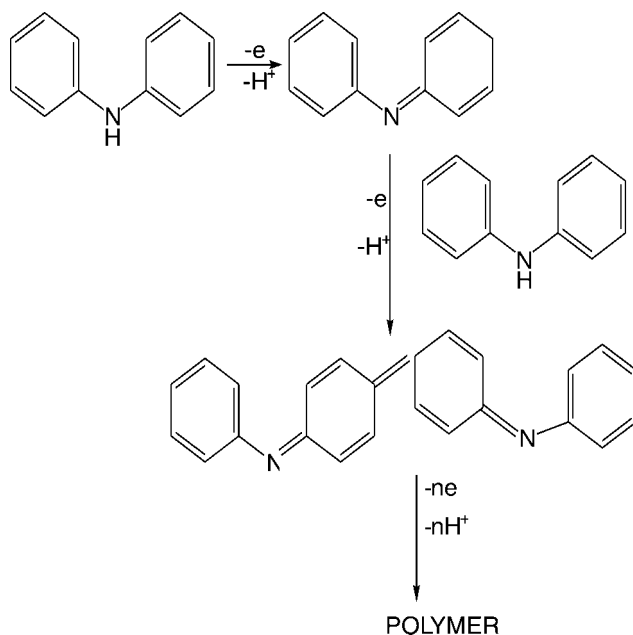


Figure 4 FTIR spectra of polydiphenylamine.



Scheme 1 Structure of polydiphenylamine.



Scheme 2 Polymerization mechanism of diphenylamine.

RESULTS AND DISCUSSION

XRD studies

The XRD pattern of PDPA is shown in Figure 3. The pattern is similar to that observed for polyaniline and intense peak at 20–25° has a similar profile as reported in literature.²⁵

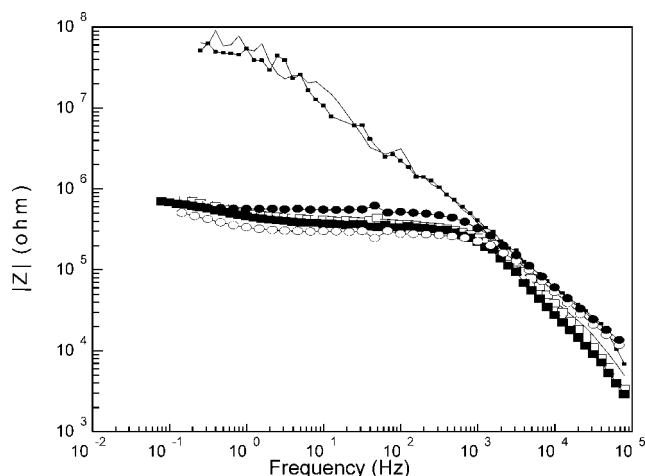


Figure 5 Impedance plots of paint coating containing 0% PDPA on steel in 0.1N HCl. Initial: ■-1 day; □-4 days; ■-7 days; ○-25 days; ●-75 days.

TABLE I
Impedance Parameters of Paint Coating Containing 0% PDPA on Steel in 0.1N HCl

Time (days)	R_c ($\Omega \text{ cm}^2$)	Y_0 ($\Omega^{-1} \text{ s}^n$)	n	C_c (F cm^{-2})
Initial	7.79×10^7	1.39×10^{-9}	0.88	1.04×10^{-9}
1	5.69×10^7	1.94×10^{-9}	0.82	1.18×10^{-9}
4	5.04×10^5	4.32×10^{-10}	1	4.32×10^{-10}
7	3.11×10^5	5.56×10^{-10}	1	5.56×10^{-10}
25	2.87×10^5	1.19×10^{-9}	0.86	3.42×10^{-10}
75	5.78×10^5	1.11×10^{-9}	0.86	3.36×10^{-10}

Fourier transform infrared spectra

The FTIR spectra of PDPA are shown in Figure 4. The spectra is very much similar to that of polyaniline¹⁹: (i) bands at 1562 and 1475 cm^{-1} are assigned to nitrogen quinone (Q) and benzenoid ring B;^{26,27} (ii) band at 1299 cm^{-1} to C—N stretch of a secondary aromatic amine; (iii) band at 876 cm^{-1} to out of plane bending of aromatic C—H; (iv) band at 799 cm^{-1} to 1,4 substituted benzene; and (v) a strong band at 1114 cm^{-1} can be explained as an electronic band or a vibration band of nitrogen in quinone. The structure of PDPA will be as given in Scheme 1.²⁸

The mechanism of polymerization has been shown by cyclicvoltammetry²⁹ as ECE mechanism consisting of a fast one electron oxidation followed by coupling of the cation radical to the C—C *para*-coupled dimer diphenylbenzidine, DPBH_2 , and subsequent oxidation to PDPA as given in Scheme 2.

EIS evaluation of coatings

The corrosion protection performance of PDPA containing coating has been evaluated by EIS. The corrosion protection ability of the coating containing 0, 1, 3,

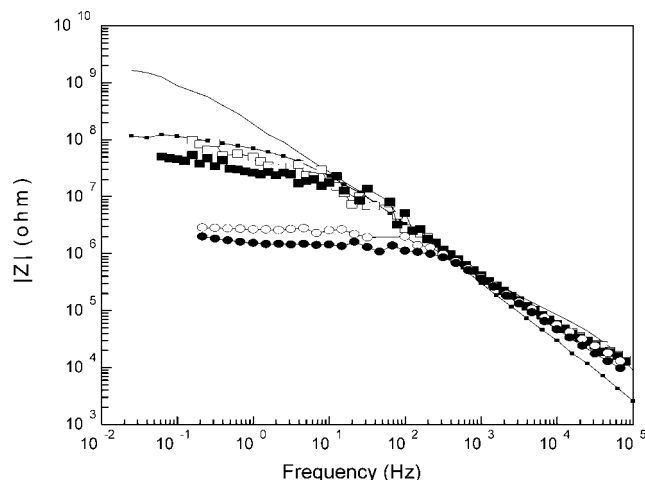


Figure 6 Impedance plots of paint coating containing 1% PDPA on steel in 0.1N HCl. Initial: ■-1 day; □-4 days; ■-7 days; ○-25 days; ●-75 days.

TABLE II
Impedance Parameters of Paint Coating Containing 1% PDPA on Steel in 0.1N HCl

Time (days)	R_c ($\Omega \text{ cm}^2$)	Y_0 ($\Omega^{-1} \text{ s}^n$)	n	C_c (F cm^{-2})
Initial	1.09×10^9	1.44×10^{-10}	0.86	8.37×10^{-10}
1	1.05×10^8	2.24×10^{-9}	0.97	6.77×10^{-10}
4	9.68×10^7	1.55×10^{-10}	0.83	1.04×10^{-10}
7	4.49×10^7	1.09×10^{-9}	0.86	6.79×10^{-10}
25	2.83×10^6	1.28×10^{-9}	0.86	5.02×10^{-10}
75	1.67×10^5	9.30×10^{-10}	0.90	4.61×10^{-10}

and 5% PDPA in vinyl binder on steel has been found out in 0.1N HCl. Figure 5 shows the impedance behavior of coating on steel without PDPA in 0.1N HCl. The resistance and capacitance values of the coating with different period of immersion are given in Table I. Initially, the resistance of the coating is $7.8 \times 10^7 \Omega \text{ cm}^2$. The resistance value is decreased with the immersion time. The resistance value is decreased to $2.5 \times 10^5 \Omega \text{ cm}^2$ after 3 days immersion and remained constant up to 75 days of immersion. The coating without PDPA is found to be less protective since the resistance value is below that of threshold value of $10^7 \Omega \text{ cm}^2$.³⁰ However, the capacitance values of the coating are remained constant in the range of $10^{-9} \text{ F cm}^{-2}$, which shows that the delamination of the coating is minimum.

The variation of impedance values for the coating containing 1% PDPA is shown in Figure 6 and the impedance parameters are given in Table II. The resistance of the coating has been found to decrease from 1.1×10^9 to $1.7 \times 10^6 \Omega \text{ cm}^2$ after 75 days immersion in 0.1N HCl. On comparing the resistance value with that of coating without PDPA, it is one order high. However this value is also less than that of threshold value of $10^7 \Omega \text{ cm}^2$. The capacitance values of the coat-

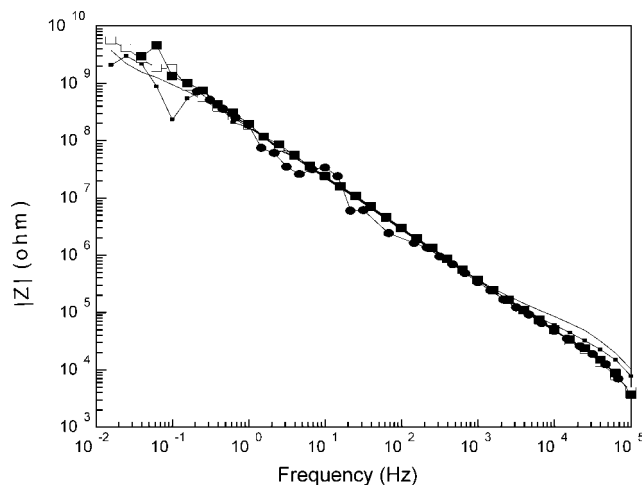


Figure 7 Impedance plots of paint coating containing 3% PDPA on steel in 0.1N HCl. Initial: ■-1 day; □-4 days; ■-7 days; ○-25 days; ●-75 days.

TABLE III
Impedance Parameters of Paint Coating Containing 3% PDPA on Steel in 0.1N HCl

Time (days)	R_c ($\Omega \text{ cm}^2$)	Y_0 ($\Omega^{-1} \text{ s}^n$)	n	C_c (F cm^{-2})
Initial	3.76×10^9	1.61×10^{-9}	0.84	2.00×10^{-9}
1	1.86×10^9	1.34×10^{-9}	0.87	1.15×10^{-9}
4	1.43×10^9	8.39×10^{-10}	0.91	5.00×10^{-9}
7	2.84×10^9	1.39×10^{-10}	0.90	9.84×10^{-10}
25	2.07×10^9	1.19×10^{-10}	0.89	3.42×10^{-10}
75	1.26×10^9	8.34×10^{-10}	0.91	1.05×10^{-10}

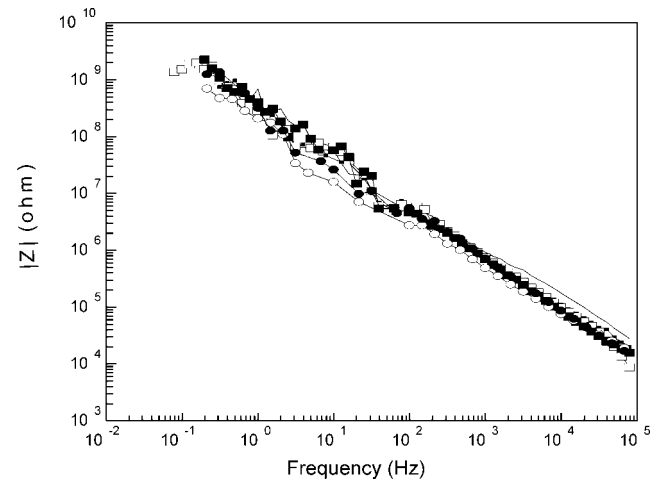


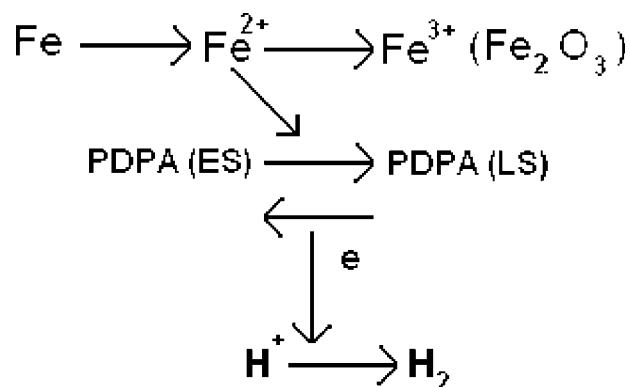
Figure 8 Impedance plots of paint coating containing 5% PDPA on steel in 0.1N HCl. Initial: ■-1 day; □-4 days; ■-7 days; ○-25 days; ●-75 days.

ing are remained in the range of $1-9 \times 10^{-10} \text{ F cm}^{-2}$ because of the absence of delamination of the coating.

The impedance parameters derived from the impedance plot (Fig. 7) of the coating containing 3% PDPA are given in Table III. The resistance values of the coating have not changed markedly with the period of immersion and remained at $10^9 \Omega \text{ cm}^2$. The capacitance values are remained at $10^{-10} \text{ F cm}^{-2}$, which indicates that the delamination of coating has not occurred. The high values of the resistance of the coating indicate the corrosion protective nature of the coating.

TABLE IV
Impedance Parameters of Paint Coating Containing 5% PDPA on Steel in 0.1N HCl

Time (days)	R_c ($\Omega \text{ cm}^2$)	Y_0 ($\Omega^{-1} \text{ s}^n$)	n	C_c (F cm^{-2})
Initial	9.55×10^9	3.79×10^{-10}	0.88	4.54×10^{-10}
1	5.41×10^9	5.54×10^{-10}	0.88	6.46×10^{-10}
4	2.58×10^9	4.07×10^{-10}	0.92	4.08×10^{-10}
7	5.34×10^9	3.57×10^{-10}	0.93	3.74×10^{-10}
25	6.76×10^9	9.10×10^{-10}	0.86	1.23×10^{-9}
75	6.41×10^9	3.14×10^{-10}	0.95	3.26×10^{-10}



Scheme 3 Protection mechanism of iron by PDPA.

Figure 8 shows the impedance variation of the coating containing 5% PDPA and Table IV gives the impedance values. It can be seen that the coating resistance values are remained constant in the range of $2.6\text{--}9.6 \times 10^9 \Omega \text{ cm}^2$ during the period of study. The capacitance values of the coatings are in the range of $1.2\text{--}6.5 \times 10^{-10} \text{ F cm}^{-2}$. These high resistance value of the coating indicates the corrosion protective nature of the coating.

The results of this study indicate that the coatings containing 3% and above of PDPA are able to protect steel in 0.1N HCl media. At lower percentage, the PDPA is not able to offer protection. The mechanism of corrosion protection by PDPA in the coating is similar to that of the protective nature of polyaniline.^{7,12,14,15} The redox property of PDPA of the reaction



has been established by cyclic voltammetric studies of PDPA film in HCl medium and the redox potential is found to be +0.850 V vs. SCE.²¹

PDPA behaves like polyaniline and due to its redox properties, it ennoble the surface of iron to the potential of formation of thin metal oxide layer. The mechanism of protection of iron by PDPA is as follows:

The emeraldine salt (ES) of PDPA is able to oxidize ferrous ions produced in the pinholes into passive iron oxide. During redox reaction, the ES of PDPA is reduced to Leuco salt (LS). The converted LS of PDPA is oxidized to PDPA-ES by the reduction of H^+ ions present in the solution to H_2 on the PDPA coated surface. The protection mechanism of iron by PDPA can be summarized in the schematic description (Scheme 3).

CONCLUSIONS

The PDPA can be prepared by the chemical oxidative method. The FTIR spectrum of PDPA shows that the

structure has got quinone and benzenoid groups in the molecule, similar to that of polyaniline. Coatings containing 3% and above of PDPA are able to offer very high corrosion protection in 0.1N HCl media. The mechanism of corrosion protection by PDPA is due to its redox property.

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