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Studies On The Synthesis And Curing Of Thermosetting Novolac Resin Using Renewable Resource Material

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Abstract: Cardanol furfural based novolac resins were synthesized using four different mole ratios in presence of an acid catalyst. The reaction was performed at 120^0C. The progress of the reaction was monitored by determining the free furfural and free phenol content. The prepared cardanol furfural resins were further characterized by various characterization techniques such as infrared and nuclear magnetic resonance spectroscopic analysis. The resins were cured by using the most suitable curing agent, hexamethylenetetramine (HMTA). Differential scanning calorimetric (DSC) technique was used to investigate the curing behavior of the prepared samples. The prepared cardanol resin has the potential to minimize the use of phenol resin based on petrochemical derivative.

Keywords: Renewable resource, Cardanol, Furfural, FTIR, NMR, DSC.

1. Introduction

Renewable resources have been the subject of keen interest among both academic and industrial researchers throughout the world at all times [1-5]. Among the renewable resources, cashew nut shell liquid (CNSL), an agricultural renewable resource material obtained as a byproduct of the cashew industry is unique in that it contains a natural phenolic distillate, cardanol [6]. Cardanol, a natural meta substituted alkyl phenol from Cashew Nut Shell Liquid (CNSL), can be regarded as a versatile and valuable raw material for polymer production [7-10] and like phenol, it can be condensed with active hydrogen containing compounds to yield a series of phenolic resins, for instance, base catalyzed resoles and acid catalyzed novolacs [9]. Resins derived from CNSL/Cardanol are widely employed in the field of surface coatings, adhesives, laminates and have several miscellaneous applications [11].

Furfural, the heteroaryl aldehyde is obtained as an agricultural waste product which has an extensive application in the formation of resins [12].

Currently, succinic acid is becoming a renewable resource synthesized by fermentation [13]. Novolac resins based on phenol-furfural, phenol-formaldehyde have already been discussed in detail by various workers [14-17] which were considered to be toxic and harmful for the environment. The synthesis of cardanol formaldehyde resins have been reported earlier [18-20] and gained much importance in the past due to their wide range of applications in composite matrix, surface coating etc. Therefore, these cardanol formaldehyde resins may further be modified by replacing formaldehyde with furfural in presence of suitable catalyst to duplicate the performance of such cardanol novolacs. Moreover, the literature pertaining to the study of cardanol furfural resins have been very rarely investigated so far, hence, the present work is concerned with the synthesis, characterization of cardanol furfural resin (*CFNR*) and its cure characteristics.

2. Experimental

2.1 Materials

Cardanol was procured from M/s Dheer Gramodyog Ltd. Kanpur, India. Furfural (A.R. grade) was obtained from Qualikems Fine Chemicals Pvt. Ltd., New Delhi was used for formylation. Succinic Acid and Hexamethylenetetraamine (HMTA) were received from Central Drug House Ltd. (CDH), Mumbai and New Delhi respectively. Methanol (BDH) was used to dissolve the free catalyst.

2.2 Methods

2.2.1 Synthesis of Cardanol- Furfural Novolac Resin

Cardanol-furfural novolac resins were synthesized from cardanol and furfural in the mole ratios viz.1:0.5, 1:0.6, 1:0.7, and 1:0.8 using succinic acid as catalyst by a method published in the literature for cardanol formaldehyde resin [21]. The catalyst (1% based on cardanol) was dissolved in 4 ml methanol under warm conditions. Cardanol was taken in three–necked round bottomed flask and furfural was added dropwise to the cardanol through a dropping funnel along with the catalyst solution. The reaction mixture was heated under constant stirring at a temperature of 120^0C which might have resulted in the formation of multinuclear cardanol-furfural resin. The initial pH value of the mixture was 4 which was reduced to 2 after completion of condensation.

2.2.2 Curing Of Cardanol-Furfural Novolac Resin

A process mentioned elsewhere [22] was adopted for curing of cardanol novolac resin by using 15 % Hexamethylenetetramine (HMTA) in preheated air oven. Hexamethylenetetramine (HMTA) is the most widely used curing agent for curing processes of novolac resins [23-24].

2.3 Characterization of Cardanol Furfural Resin

2.3.1 Fourier-Transform Infra-Red (FTIR) Spectroscopic Analysis

The purified resin was subjected to Fourier-transform infra-red (FTIR) spectroscopic analysis, to monitor the formation or disappearance of various functional groups using Perkin-Elmer (Model 843) infra-red spectrophotometer in the wavelength range of 500-4000 cm^{-1}. Potassium bromide (KBr) pellets were used to get the spectra of uncured material.

2.3.2. ^{1}HNMR Spectroscopic Analysis

^{1}H-NMR (Nuclear Magnetic Resonance) of the purified novolac resin was recorded using Jeol-LA 500 NMR spectrophotometer. About 20 mg of the sample, in 10 mm diameter sample tube, was dissolved in about 5ml of chloroform-d1 (CDCl3) which was used a solvent along with tetramethylsilane (TMS) as internal standard. Finally, the spectra were recorded on computer.

2.3.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetric (DSC) analysis of the prepared samples were carried out to investigate the curing behavior of the cardanol furfural resins.Cure temperature of the prepared samples were observed by taking a small amount of sample into shallow aluminium pan sealed by an aluminium cover of differential scanning calorimeter (DSC) (TA instrument, USA; Modulated DSC-2920). This was placed in sample cell of the instrument; the starting temperature, programmed rate and final temperature were taken at heating rate of 10^oC.min-^{1}. Dynamic scans were obtained which were used for assuming the cure temperature.

3. Result and Discussion

3.1 Synthesis of Cardanol-Furfural Novolac Type Phenolic Resin

The methylolation of cardanol was carried out with furfural in presence of dicarboxylic acid, viz., succinic acid using four different mole ratios. The completion of the methylolation reaction was checked by the periodic withdrawal of reaction mixture to analyze free furfural content and free phenol content.

The polymerization of cardanol can be accomplished in two ways, firstly, by the condensation of furfural and, secondly, through the unsaturation present in the side chain. The side chain of cardanol remained unaffected because it is clear from the measure of iodine value [25]. The iodine value of cardanol before polymerization was 278.8wijs and after polymerization the iodine value of the reaction product was found to be 278.2. Therefore, it is concluded that the polymerization proceeded by the first way, i.e. by the complicated step growth polymerization reaction mechanism [26].The proposed mechanism of the reaction between cardanol and furfural was based on the literature published earlier [27]. The structure of cardanol furfural resin have been represented in Scheme [1].

3.3 Fourier-Transform Infra-Red (FTIR) Spectroscopic Analysis

Fig.1 depicted the FTIR spectrum cardanol-furfural novolac type phenolic resin (sample *CFNR*$_5$) and explored not only the condensation reaction of cardanol furfural but also the extent of ortho and para substitution. A broad peak centered at 3392 cm^{-1} was appeared in the spectrum (Fig.1) confirmed the presence the phenolic hydroxyl group in the resinous product. The peaks that appeared near 3010 cm^{-1} and 2927 cm^{-1} might be due to the presence of aromatic CH stretching and aliphatic CH stretching, respectively, present in the side chain of cardanol. The stretching vibrations near 2927 cm^{-1} and 2855 cm^{-1} and deformative vibrations near 1488 cm^{-1} and 1457 cm^{-1} might be due to the presence of CH_2 and CH_3 groups, respectively in Fig.1. These above mentioned peaks due to stretching and deformative vibration indicated that the polymerization has taken place through the substitution of $-CH_2OH$ and not through the double bonds in the side chain. The sharp band near 2854 cm^{-1} might be due to the C-H structure in a methylene bridge in Fig.1, which might form due to the condensation reaction between cardanol and furfural. The sharp peaks near 728 cm^{-1} and 873 cm^{-1} indicated ortho and para substitution in benzene nuclei respectively. A peak near 1266 cm^{-1} might correspond to phenol C-O stretching. The preceding spectral data were found to be identical with those given in the literature [28].

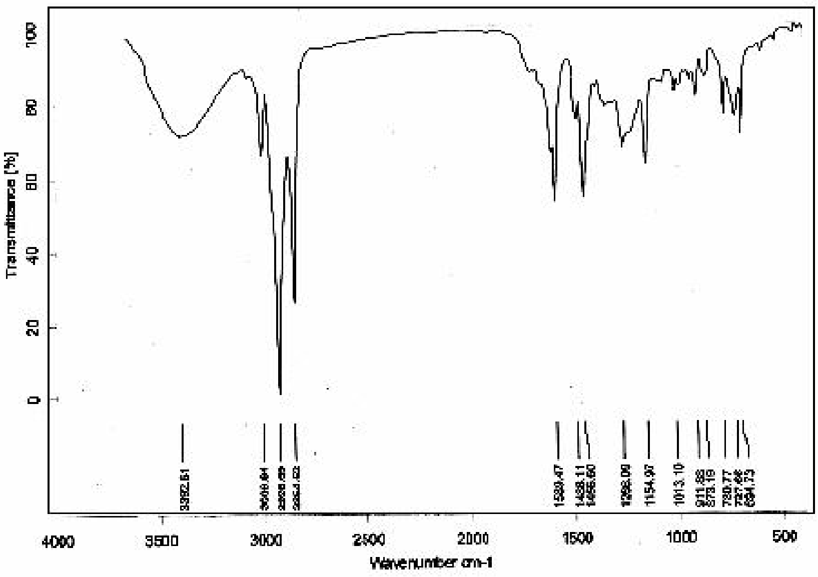


Fig. 1: FTIR Spectrum of cardanol furfural resin, *CFNR*$_5$

3.4 ^{1}H-NMR Spectroscopic Analysis

^{1}H-NMR (Nuclear Magnetic Resonance) of the purified novolac resin was recorded using Jeol-LA 500 NMR spectrometer. In the ^{1}H-NMR spectrum of cardanol furfural resin (Fig.2 sample *CFNR*$_5$), the appearance of a peak at 6.6-7.3 ppm is due to aromatic protons of benzene and furan ring. The peak around the region 6.6 ppm might be due to the presence of phenolic hydroxyl group. The peak at 4.7-5.4 ppm indicated the methylene ($C=CH_2$) proton of long alkyl side chain originally present in cardanol and the peak at 0.8-2.9 ppm is due to long aliphatic side chain. The peak at 0.9 ppm might be due to terminal methyl group of the chain. The strong peak at 1.3 ppm is attributed to the long chain (more than five methylene groups) of the side chain. The peak at 2.8 ppm showed the methane proton of $(C_6H_5)_2$-CH-C_4H_3O for the bridge between two phenyl rings and one furan ring. All these spectral data indicated that condensation of methylolated cardanol with furfural, has been completed under experimental conditions and was fully consistent with the proposed structure [Scheme 1] resulted due to reaction mechanism as discussed in our previous publication [28].

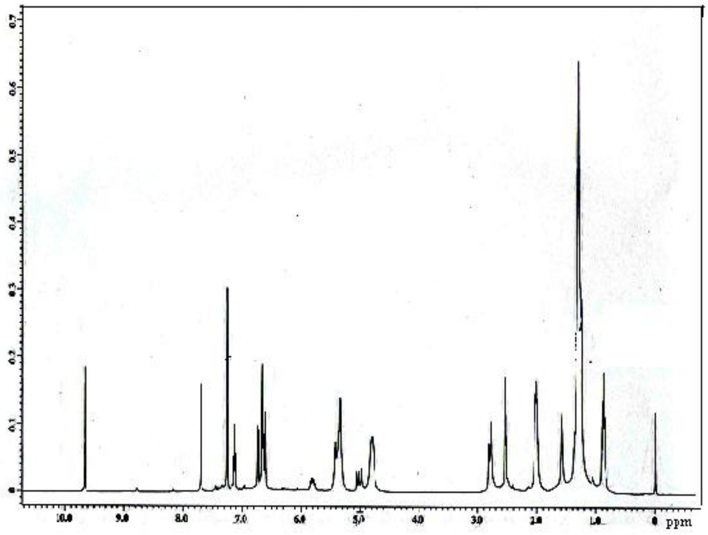


Fig. 2: ^{1}H-NMR Spectrum of cardanol furfural resin, *CFNR*$_5$

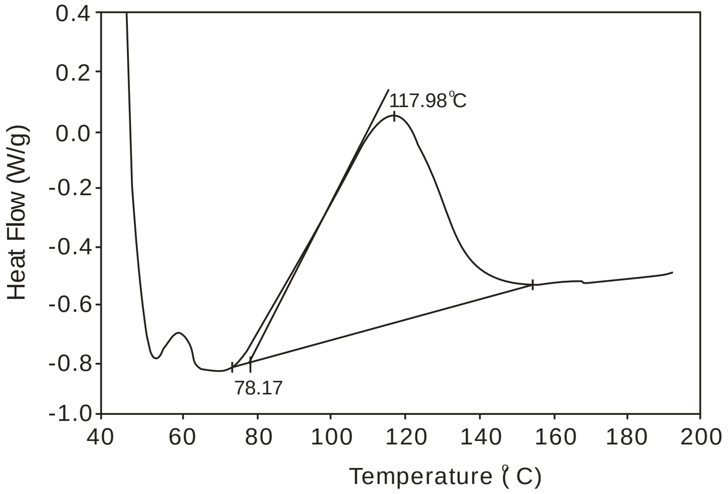
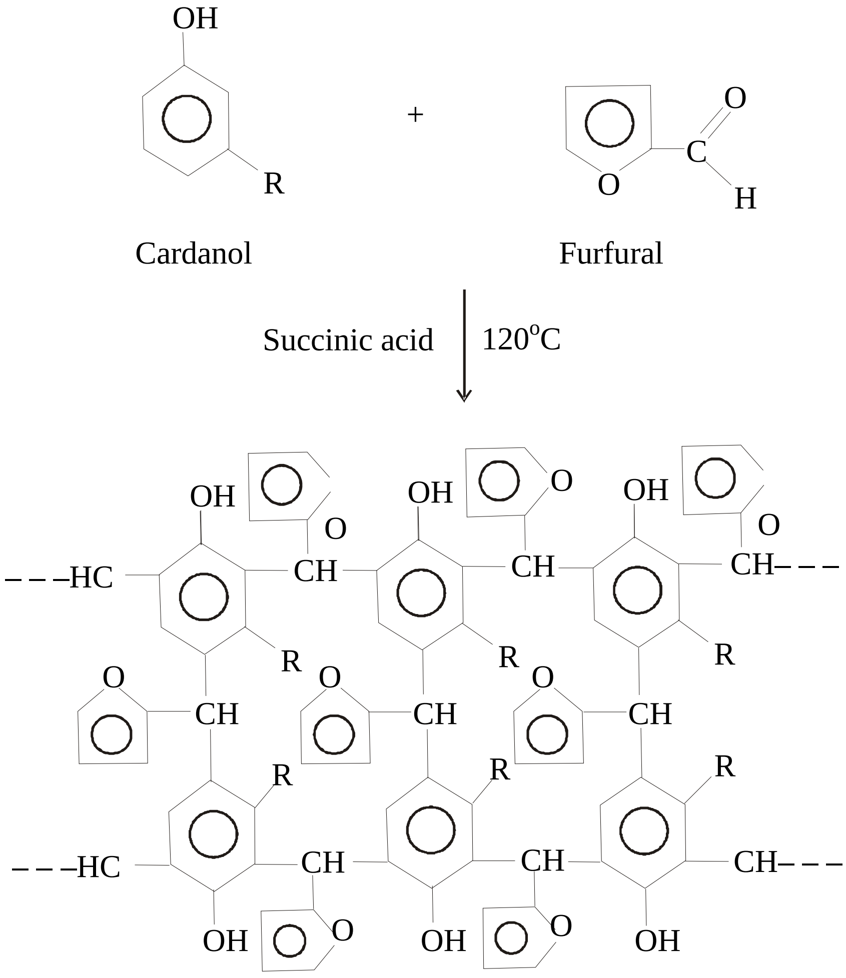


Fig. 3: Dynamic DSC Scan of sample, *CFNR*$_5$



Scheme 1: Structure of cardanol furfural resin

3.5 Differential Scanning calorimetric analysis for curing of *CFNR*

The temperature of onset (T_i), peak temperature (T_p) and the temperature of completion of the exotherm (T_{stop}) were noted from the Fig. 3 (Sample, $CFNR_5$) and the data related to the dynamic DSC scans of $CFNR_5$, $CFNR_6$, $CFNR_7$ and $CFNR_8$ respectively, are summarized in Table 1. It is evident from the table that the initiation of crosslinking reaction lied in the range of 75.17-98.25 ^{o}C with peak maximum temperature 137.87, 142.12, 148.42 and 153.98 ^{o}C for samples $CFNR_5$, $CFNR_6$, $CFNR_7$ and $CFNR_8$, respectively. The completion of exotherm was observed in the range of 182.32-169.91 ^{o}C. The ΔH values related to the cure process were determined from the area of the exotherm peak obtained from DSC analysis taken in dynamic mode. The preceding data and results of DSC dynamic scan were found to be in agreement with the given literature [25]. The curing of all the novolac samples were completed in an air oven using hexamethylenetetramine. All of the samples were cured at 160°C but at different time intervals [Table 2].

4. Conclusions

This proposed research may lead to a new era in the field of cardanol resins. The modified cardanol furfural resin has the potential to minimize the use of phenol resin based on petrochemical derivative. Moreover, Furfural, being a product of vegetable origin and available in virtually unlimited quantities, is much more economical aldehyde than formaldehyde. The prepared resin system finds numerous applications in composite matrix, surface coatings, brake linings, lamination industry, pesticides, azodyes etc.

Table 1: Results obtained from Dynamic DSC scan

S.No.	Samples	T_i [a] (°C)	T_p [b] (°C)	T_{stop} [c] (°C)	ΔH (Jg^{-1})
1	***$CFNR_5$***	**75.17**	**137.87**	**169.91**	**98.26**
2	***$CFNR_6$***	**98.25**	**142.12**	**177.16**	**108.11**
3	***$CFNR_7$***	**112.81**	**148.42**	**182.32**	**123.61**
4	***$CFNR_8$***	**121.31**	**153.98**	**186.48**	**85.90**

T_i represents temperature of onset; T_p peak temperature; T_{stop} temperature of completion of the exotherm;
[a] Temperature of cure initiation; [b]Temperature of cure maximum; [c] Temperature of end of cure.

Table 2 : Study of Cure Schedule

S.No.	Samples	Cardanol:furfual (mole ratio)	Cure Time (min)	Cure Temperature (°C)
1	*$CFNR_5$*	1.0:0.5	90	160
2	*$CFNR_6$*	1.0:0.6	115	160
3	*$CFNR_7$*	1.0:0.7	150	160
4	*$CFNR_8$*	1.0:0.8	180	160

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References

[1]. Sperling L.H., Manson J.A., Quresh S. and Fernandez A.M., Tough plastics and reinforced polymers from renewable resource industrial oils, Ind. Eng. Chem. Prod. Res. Dev.,1981, 20,163-166.

[2]. Chen Y., Zhang L. and Du L., Structure and Properties of composites compression molded from polyurethane prepolymer and various soy products, Ind. Eng. Chem. Res., 2003, 42,6786-6794.

[3]. Anastas P. T., Kirchhoff M. M., Origins, current status, and future challenges of green chemistry, Acc. Chem. Res., 2002, 35, 686-694.

[4]. Hoefer R., Daute P., Gruetzmacher R. and Westfechtel A., Oleochemical polyols A new material source for polyurethane coatings and floorings , J. Coat. Technol., 1997, 69, 65-72.

[5]. Maffezzoli A. and Calo E., Cardanol based matrix biocomposites reinforced with natural fibers Compos Sci Technol , 2004, 64, 839-845.

[6]. Tyman J.H.P., Johnson R.A., Muir M. and Rokhgar R., The extraction of natural cashew nut-shell liquid from the cashew nut *(*Anacardium occidentale*)*, J. Am. Oil. Chem. Soc., 1989, 66, 553-557.

[7]. Patel M.S., Patel V.S. and Patel R.G., Effects of reactive diluent diepoxidized cardanol and epoxy fortifier on curing kinetics of epoxy resin, J. Therm. Anal., 1989, 35, 47-57.

[8]. Pillot J. P., Vanthanh M.D.M., Gerval J. and Dunogues J., Hydrosilylation of cardanol by methyldichlorosilane-application to the synthesis of new silicone grafted phenolic resins , Euro. Poly. J., 1989, 25, 285-289.

[9]. Manjula S., Pavithran C., Pillai C.K.S. and Kumar V.G., Synthesis and mechanical properties of cardanol-formaldehyde (CF) resins and CF-poly(methylmethacrylate) semi-interpenetrating polymer networks, J. Mater. Sci., 26, 4001-4007.

[10]. Manjula S., Kumar V.G. and Pillai C.K.S., Kinetics and mechanism of oligomerization of cardanol using acid catalysts, J. Appl. Polym. Sci., 1992, 45, 309-315.

[11]. Emanuel A. L. and Sinha V.K., Cashew nut shell liquid resin composites reinforced by sawdust and wood flake, Praj. J. Pure & Appl. Sci., 2008, 16, 16-29.

[12]. Brown L.H., Resin Forming Reactions of Furfural and Phenol, Ind. Eng. Chem., 1952, 44, 2672-2675.

[13]. Das T.K., Das D., Guru B.N., Das K.N. and Lenka S., Polymers from Renewable Resources XXVIII Synthesis, Characterization and Thermal Studies of Semi-Interpenetrating Polymer Networks Derived from Castor Oil based Polyurethanes and Cardanol Derivatives, Polym. Plast. Technol. Eng. , 1998, 37,427-435.

[14]. Su Z., Li Y., Miao Y., Wang T. and Pu Q., Preparation and characterization of macroporous phenol-furfural sulfonic acid resin catalyst, J. Appl. Polym. Sci., 1764,80 ,1764-1769.

[15]. Kierkels R.HM., Kempen B.V., Geleen C.H.M., Baur H.A.C (1994) United States Patent ;5359024.

[16]. Hickson H, Albany N. (1981) Phenol formaldehyde resin for hardboard applications. United States Patent ; 4269949.

[17]. Kim S., Kim H.S., Kim H.J. and Yang H.S., Fast curing PF resins mixed with various resins and accelerators for building composite materials, Const. build. Mat. 2008, 22, 2141-2146.

[18]. Sathyalekshmi K. and Gopalakrishnan S., Synthesis and characterization of rigid polyurethanes based on hydroxyalkylated cardanol formaldehyde resin, Plast. Rub. Compos .,2000, 29, 63-69.

19]. Mythili C.V., Retna A. M. and Gopalakrishnan S., Synthesis, mechanical, thermal and chemical properties of polyurethanes based on cardanol, Bull. Mater . Sci., 2004, 27, 235-241.

20]. Kattimuttathu I. S. and Vadi S.K., Synthesis, Structure, and Properties of Novel Polyols from Cardanol and Developed Polyurethanes, Ind. Eng. Chem. Res., 2005, 44, 4504-4512.

[21]. Devi A. and Srivastava D., Cardanol-based novolac-type phenolic resins. I. A Kinetic approach , J. Appl. Polym. Sci., 2000, 2730-2737.

[22]. Raquez J.M., Deliglise M., Lacrampe M.F. and Krawczak P., Thermosetting (bio) materials derived from renewable resources: A critical review, Prog. In. Polym. Sci., 2010, 35, 487-509.

[23]. Zhang X., Looney M.G., Solomon D.H. and Whittaker A.K., The chemistry of novolac resins 3 C-13 and N-15 nmr studies of curing with hexamethylenetetramine, Polym., 1997,38, 5835-5848.

[24]. Knop A. and Pilato L.A., Chemistry and Application of Phenolic Resins, Springer- Verlag, Berlin,1985.

[25]. Nair C.P.R., Bindu R.L. and Joseph V.C., Cyanate esters based on cardanol modified –phenol-formaldehyde resins- synthesis and thermal characteristics, J. Polym. Sci. Part A Polym. Chem., 1995, 33: 621-627.

[26]. Mishra D.K., Mishra B.K., Lenka S. and Nayak P.L., Polymers from renewable resources. VII: Thermal properties of the semi-interpenetrating polymer networks composed of castor oil polyurethanes and cardanol-furfural resin, Polym. Engin. Sci., 1996, 36, 1047-1051.

[27]. Kuriakosa A.P. and Manjooran S.K.B., Bitumenous paints from refinery sludge., Surf .Coat. Tech., 2001,145, 132-138.

[28]. Martin R.W., The Chemistry of Phenolic Resins, John Wiley & Sons,28,1956.

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