"Effect Of Functional Group Of Additives On The Dielectric Properties Of Polyvinyl Alcohol Films"

HK Mahavar*

*Department of Physics, MSJ Govt. P.G. College, Bharatpur, Rajasthan, India-321001

*Corresponding Author: HK Mahavar

Abstract

The major aim of this study is to obtain a wide range of the dielectric properties of PVA films filled with different functional group of additives in order to select the suitable set of functional group necessary for the technical applications. The dielectric measurements on virgin PVA and its composite films with functional group of additives are performed at 9.035 GHz frequency and at temperature range 305K-385K.

The dielectric parameters like $\epsilon', \epsilon'', \sigma, \tau, \tan \delta$, k and n depend on the number of functional groups present in the polymeric film as an additives. The temperature dependence of ϵ' for all investigated samples is insignificant but presence of dopants in the film samples significantly affects the parameter ϵ' .All the results obtained from various parameters of PVA and doped PVA with functional group of additive films, clearly show that the presence of the number of functional group in the PVA lattice significantly affect the physical properties of the virgin PVA film.

Keywords: PVA, OA, MA, TA, CA, Dielectric parameters, XRD, DSC, T_{g} , E_{a}

1. INTRODUCTION

In the present era million tons of plastics are produced annually all over the world and it continues to increase because of the successive enhancement in the rate of consumption. These are used in many area of manufacturing and have naturally found application in the construction of electronic devices.

The dielectric properties of polymeric films are of direct interest to both the basic studies of electrical conduction through such films and their application in capacitors for microelectronics [1]. Extensive observations have been made by several workers to study the molecular motion and the charge carrier migration in a variety of polar/nonpolar linear polymers containing one or more than one active groups in the same monomer unit [2-4]. The dielectric constant and dissipation factor are the crucial quantities in the design of a device. These quantities are invaluable to engineers in their design of microelectronic equipment. The physicists are more interested in the microscopic processes responsible for the dielectric relaxation. Moreover, the study of dielectric constant and dielectric loss factor, as a function of temperature and frequency is one of the most convenient and sensitive methods of studying the polymer structure [5] of a polymeric film.

In the recent years the dielectric properties of a number of polymers have been investigated [6-8]. Considerable attention has been devoted to the problems of the change in the dielectric properties in polymers due to intentional doping [7-10]. The charge carrier mobility can be greatly influenced by impregnating the polymers with suitable dopants [11], depending on their chemical structure and the way in which they interact with the macromolecular matrix.

In this study, the dielectric properties of polyvinyl alcohol (PVA) films, filled with different functional group of additives were compared. Oxalic acid (OA) with 2 carboxyl group, Malic acid (MA) with 1 hydroxyl and 2 carboxyl group, Tartaric acid (TA) with 2 hydroxyl and 2 carboxyl group and citric acid (CA) with 1 hydroxyl and 3 carboxyl group were used as additives. The structure of PVA and each additive are represented in Figure 1.

The present work describes the results of our investigations over dielectric properties of PVA films filled with different group of additives in the microwave X- band frequency range and at different temperatures. The major aim of this study is to obtain a wide range of the dielectric properties of PVA films filled with different functional group of additives in order to select the suitable set of functional group necessary for the technical applications.

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Figure 1: Chemical structures of the (a) Polyvinyl alcohol (b) OA, (c) MA, (d) TA, (e) CA

2. EXPERIMENTAL

Sample Preparation

PVA (MW: 1,25,000 amu), OA, MA and CA were obtained from Central Drug House (P) Ltd., New Delhi (India), while TA was purchased from Qualigens Fine Chemicals (Glaxo India Limited) Mumbai (India), the synthesis of films having thickness of the order of 100 μ m for virgin PVA and filled with 5% by weight of OA, MA, TA and CA were carried out using solution cast method [10,12-14]. The thickness of the film was determined using micrometer (Mitutoya, Japan,

M120-25) with a least count of 1 μ m, at different places in each film and an average was taken which was found of the order of 100 μ m.

Theory and Experimental Technique

The prepared films of pure PVA and doped PVA with functional group of additives were subjected for the measurement of their dielectric parameters at microwave frequencies and at different temperatures using the techniques developed by Dube and Natarajan [15-16].



Figure 2:- Experimental set up in X-band for films with temperature arrangement

The advantage of this method is that the specimen is placed longitudinally at the centre of broad side of a hollow rectangular waveguide excited in the TE₁₀ mode, so that the entire specimen remains in the maximum electric field. Standing waves were produced in the rectangular waveguide by short circuiting the system and detected in the slotted line by means of a travelling wave detector for the measurement of dielectric parameters. A selfdesigned temperature control unit arrangement was used to vary and maintained the temperature of the specimen during the measurement of microwave data (Fig.2), the accuracy of the temperature control unit is 0.1^0 .

The dielectric permittivity ϵ' and dielectric loss ϵ'' were calculated by measuring the shift in minima and voltage standing wave ratio (VSWR) without and with the specimen. These microwave data so collected was employed to determine relaxation time (τ) and loss tangent (tan δ) respectively, using the following equations:

$$\tau = \frac{\epsilon^{*}}{\omega \epsilon'} \qquad \dots (1)$$
$$\tan \delta = \frac{\epsilon^{"}}{\epsilon'} \qquad \dots (2)$$

and the conductivity of the specimen was determined using the relations

$$\sigma' = \omega \epsilon_0 \epsilon^{"} \qquad \dots (3)$$

$$\sigma^{"} = \omega \epsilon_0 \epsilon' \qquad \dots (4)$$

where σ' and σ'' are, respectively the real and imaginary part of the conductivity, $\sigma = \sigma' + i\sigma''$. The real part of conductivity (dielectric conductivity) shows the features of ac conductivity in composite materials [13,14,17].

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The optical constants like extinction coefficient (k) and refractive index (n) have been calculated for the specimen using the relations [10,18,19]

$$\tan \delta = \frac{2k}{1-k^2} \qquad \dots (5)$$
$$\epsilon'' = 2n^2k \qquad \dots (6)$$

The significance of k is given by the fact that after the wave has travelled over a distance equal to the wavelength of wave in the dielectric material, its amplitude decays by a factor $e^{-2\pi k}$ [18].

The activation energy (E_a) for all samples was also calculated from $\ln \sigma'$ versus 1000/T curves, which follow the well-known Arrhenius law [20-22]

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{K_B T}\right) \quad \dots (7)$$

where σ_0 is a pre-exponential factor depending on the materials, E_a is the activation energy for conduction, T is the absolute temperature and K_B is the Boltzmann's constant.

3. Results and discussion

The dielectric parameters $\epsilon', \epsilon'', \sigma', \tau, \tan \delta$, k and n carried out for pure PVA and doped PVA films with 5 wt% of different functional group of additives at 9.035 GHz frequency and at different temperatures (305K–385K) have been depicted in Table 1. Figure 3 correlates the real part of dielectric constant (ϵ') and absolue temperature for pure PVA and doped PVA with functional group of additives. The behaviour of the curve reveals that the value of ϵ' , of doped PVA film increases with increasing the number of functional groups in the polymeric film. ϵ' for PVA and OA (with 2 Carboxyl group) added

films found to be 2.42, whereas ϵ' for PVA/MA (with 1 hydroxyl and 2 Carboxyl group) film is 2.51, for PVA/TA (with 2 hydroxyl and 2 Carboxyl group) film, ϵ' becomes 2.53 and for PVA/CA (with 1 hydroxyl and 3 Carboxyl group) added film ϵ' is found to be 2.54 at room temperature (305K). ϵ' for pure PVA film is found 3.08 at temperature 305K. Our results for pure PVA films are in agreement with the results reported by Raja *et al.* [20].



Figure 3:- Variation of dielectric constant (ϵ') of PVA and doped PVA with different functional group of additives

Initially ϵ' decreases from 3.08 for pure PVA to 2.42 for OA added film. The decrease in ϵ' on doping may be explained on the basis of the fact

that the incorporation of small amount (5 wt%) of dopant form charge transfer complexes in the host lattice [23].

Table 1:- Dielectric parameters of PVA and doped PVA films with different functional group of additives at 9.035 GHz. frequency and at different temperature

Sample	Dielectric	Dielectric	a.c.conductivity	Relaxation time	Loss	Extinction	Refractive
	Constant	loss	σ' (Sm ⁻¹)	τ (10 ⁻¹²) Sec.	tangent	coefficient	Index
	ϵ'	ε"			tan δ	k	n
			<u>Temp.: 305 K</u>				
PVA	3.08	0.99	0.50	5.7	0.32	0.16	1.78
PVA+5%OA	2.42	1.18	0.59	8.6	0.48	0.23	1.60
PVA+5%MA	2.51	1.23	0.62	8.7	0.49	0.23	1.63
PVA+5%TA	2.52	128	0.65	9.0	0.51	0.24	1.64
PVA+5%CA	2.54	1.5	0.73	10.0	0.57	0.26	1.65
			<u>Temp.: 315 K</u>				
PVA	3.08	1.23	0.62	7.1	0.40	0.19	1.79
PVA+5%OA	2.42	1.39	0.70	10.1	0.57	0.26	1.62
PVA+5%MA	2.51	1.50	0.76	10.6	0.60	0.28	1.65
PVA+5%TA	2.52	1.59	0.80	11.1	0.63	0.29	1.66
PVA+5%CA	2.54	1.71	0.86	11.9	0.67	0.30	1.67
			Temp.: 325 K				
PVA	3.08	1.42	0.71	8.1	0.46	0.22	1.80
PVA+5%OA	2.42	1.59	0.80	11.6	0.66	0.29	1.63
PVA+5%MA	2.51	1.68	0.84	11.8	0.67	0.30	1.66
PVA+5%TA	2.52	1.79	0.90	12.5	0.71	0.32	1.68

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PVA+5%CA	2.54	1.88	0.95	13.1	0.74	0.33	1.69
			<u>Temp.: 335 K</u>				
PVA	3.08	1.50	0.76	8.7	0.49	0.23	1.80
PVA+5%OA	2.42	1.69	0.85	12.3	0.70	0.31	1.64
PVA+5%MA	2.51	1.84	0.93	13.0	0.74	0.33	1.68
PVA+5%TA	2.52	1.98	1.00	13.9	0.79	0.35	1.69
PVA+5%CA	2.54	2.05	1.03	14.2	0.81	0.35	1.70
			<u>Temp.: 345 K</u>				
PVA	3.08	1.60	0.80	9.2	0.52	0.24	1.81
PVA+5%OA	2.42	1.89	0.95	13.7	0.78	0.34	1.66
PVA+5%MA	2.51	2.01	1.01	14.1	0.80	0.35	1.69
PVA+5%TA	2.52	2.17	1.09	15.2	0.86	0.37	1.71
PVA+5%CA	2.54	2.21	1.11	15.3	0.87	0.37	1.72
			<u>Temp.: 355 K</u>				
PVA	3.08	1.73	0.87	9.9	0.56	0.26	1.82
PVA+5%OA	2.42	2.08	1.04	15.1	0.85	0.37	1.68
PVA+5%MA	2.51	2.17	1.09	15.2	0.86	0.37	1.71
PVA+5%TA	2.52	2.26	1.13	15.8	0.90	0.38	1.72
PVA+5%CA	2.54	2.29	1.15	15.9	0.90	0.38	1.73
			<u>Temp.: 365 K</u>				
PVA	3.08	1.64	0.83	9.4	0.53	0.25	1.81
PVA+5%OA	2.42	1.79	0.90	13.0	0.74	0.33	1.65
PVA+5%MA	2.51	2.01	1.01	14.1	0.80	0.35	1.69
PVA+5%TA	2.52	2.08	1.04	14.5	0.82	0.36	1.70
PVA+5%CA	2.54	2.13	1.07	14.8	0.84	0.36	1.71
			<u>Temp.: 375 K</u>				
PVA	3.08	1.46	0.74	8.4	0.48	0.22	1.80
PVA+5%OA	2.42	1.59	0.80	11.6	0.66	0.30	1.63
PVA+5%MA	2.51	1.76	0.89	12.4	0.70	0.32	1.67
PVA+5%TA	2.52	1.89	0.95	13.2	0.75	0.33	1.68
PVA+5%CA	2.54	1.96	0.90	13.6	0.77	0.34	1.74
			<u>Temp.: 385 K</u>				
PVA	3.08	1.23	0.62	7.1	0.40	0.19	1.79
PVA+5%OA	2.42	1.49	0.75	10.9	0.61	0.28	1.62
PVA+5%MA	2.51	1.59	0.80	11.2	0.63	0.29	1.66
PVA+5%TA	2.52	1.69	0.85	11.8	0.67	0.30	1.67
PVA+5%CA	2.54	1.80	0.90	12.5	0.71	0.32	1.68

The value of ϵ' , for both hydroxyl and carboxyl group (MA, TA and CA) added films is higher than that of OA (with only 2 carboxyl group) added film and it was found to be 2.51, 2.52 and 2.54 for MA, TA and CA added films respectively at temperature 305K. It is also observed that the value of ϵ' for all the samples under investigation remain approximately uniform at the studied temperature.

Figure 4 shows the variation of dielectric loss (ϵ ") with temperature. It is observed from the figure

that ϵ " increases with the increasing content of the additives with hydroxyl and carboxyl group as a functional group. ϵ " for OA added film is lower than that of MA, TA and CA added films respectively. As the temperature increases, the ϵ " increases up to the temperature 355K, which is glass transition temperature (T_g) of PVA [24], and there after ϵ " decreases for all the investigated specimen accordingly.



Figure 4:- Variation of dielectric loss (ϵ'') of PVA and doped PVA with different functional group of additives

The higher the value of ϵ " for higher number of functional groups, present in the PVA matrix, can be understood in terms of ac conductivity (σ'), which is associated with ϵ " (Eq. 3). At low temperature hydrogen bonding is stronger between PVA and additives due to the higher availability of free polar centres, therefore conductance will be lower. Higher the number of free polar centres, lower is the conductivity. As temperature increases, hydrogen bonding

becomes weaker, makes number of free polar centres to drop and causes increase in conductance. The temperature dependence of the conductivity for all polymer electrolyte films (Fig. 5) can also be understood in terms of activation energy (E_a), which is the minimum energy required to overcome potential barrier of the system, obtained from the slopes of the plots shown in Figure 6 using the equation (7).



Figure 5:- Variation of ac conductivity (σ') of PVA and doped PVA with different functional group of additives



Figure 6:- Variation of ln(ac conductivity) vs. 1000/T plots for PVA films doped with different functional group of additives

For the film of virgin PVA, E_a is found to be 0.15 eV and for OA, MA, TA and CA added films E_a is found to be 0.14, 0.13, 0.12 and 0.11 eV respectively. The activation energy for post T_g region is found to be negative for all the sample under investigation. A negative activation energy occurred, when the rates of reaction decreases with increase in temperature. Reactions exhibiting these negative energies are typically barrier less,

in which the reaction proceeding relies on the capture of the molecules in the potential well. Increasing the temperature leads to a reduced probability of the colliding molecules, capturing one another, expressed as a reaction cross-section that decreases with increasing temperature. The calculated data for activation energies are summarized in Table 2.

Table 2:- Activation energy (Ea) and Glass transition	temperature obtained for PVA and doped PVA films
with different function	nal group of additives

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Sample	Activation energy	Glass transition temperature			
	(eV)	T_{g} (⁰ C)			
PVA	0.15	_			
PVA+5%OA	0.14	52.23			
PVA+5%MA	0.13	51.94			
PVA+5%TA	0.12	51.38			
PVA+5%CA	0.11	_			

Larger E_a values imply that the system requires a large energy to be supplied to it to break the hydrogen bonds and hence implies either a stronger hydrogen bond or the presence of large number of hydrogen bonds. As per the results found in terms of activation energies, our conductivity data as well as dielectric loss data were found accordingly, for OA added film conductivity is higher than that of pure PVA film (E_a of OA added film is lower than PVA film) and there after conductivity increases as per the order of decrease in activation energies. The ac

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conductivity at temperature 305K, for pure PVA film is found to be 0.50 Sm⁻¹, for OA added film 0.59 Sm⁻¹, MA added film 0.62 Sm⁻¹, TA added film 0.65 Sm⁻¹ and for CA added film σ' is obtained 0.73 Sm⁻¹. Higher the conductivity, lower is the activation energy. Our results are in accordance with the activation energies and conductivities (Fig. 7). Similar trend at other temperatures is observed in the data of σ' for all the specimen under investigation.



Figure 7:- Variation of activation energy and ac conductivity (at temp. 305K) of PVA films doped with different functional group of additives

The relaxation time (τ) evaluated using equation (3), for pure PVA and PVA doped films, τ is found to be of the order of pico second and in the range 5.7 to 10.0 at 305K temperature. As temperature increases, τ increases as per the order of the number of functional group, present in the polymeric matrix.

Dielectric relaxation is the exponential decay with time of the polarization in a dielectric, when an externally applied field is removed. The relaxation time may be defined as the time in which this polarization is reduced to 1/e times its original value, e being the natural logarithmic base. Dielectric relaxation is the cause of anomalous dispersion in which the dielectric constant decreases with increasing frequency. In terms of the theory of this phenomenon as developed by Debye [25], dielectric relaxation is the lag in dipole orientation behind an alternating electric field. The dielectric relaxation time (τ) for PVA and PVA doped composite film are found to be temperature dependent. The increased relaxation time in composite films is due to the intermolecular interactions between PVA and additive molecules. The value of τ are in agreement with the values reported earlier by Tanwar et al. [10,13] and Khare et al. [26]. The plot of τ with respect to temperature at varying increment of functional group for PVA and PVA doped films is shown in Figure 8.



Figure 8:- Variation of relaxation time (τ) of PVA and doped PVA with different functional group of additives

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Loss tangent (tan δ) for pure PVA and PVA doped composite films with functional group of additives has been obtained in the range 0.32-0.57 at 305 K temperature. It is also seen that as temperature increases, tan δ increases up to temperature 355K and on further increase in temperature tan δ decreases up to 385K for all the samples under investigation. The values of tan δ with respect to studied temperature for all the polymer electrolyte films are listed in Table 1. The variation of $\tan \delta$ with temperature shows similar trend for all the investigated specimen (Fig. 9). The origin of microwave dielectric loss in polymer are attributed to dipole dispersion in both crystalline and amorphous polymers, dipolar losses due to impurities and photon-phonon absorption spectra corresponding to density of states in amorphous regions of polymer [27].



Figure 9:- Variation of loss tangent (tan δ) of PVA and doped PVA with different functional group of additives

The optical constant viz. k and n have been obtained using equations (5) and (6) respectively. The variation of k and n with respect to studied temperature range 305K-385K are tabulated in Table 1. At 305K temperature, for pure PVA, k comes out to be 0.16 and for its composite films with functional group of additives, k varies in the range 0.23-0.26. The significance of k is given by the fact that after the wave has travelled over a distance equal to the wavelength of wave in the

dielectric material, its amplitude is multiplied by a factor $e^{-2\pi k}$ [18]. The value of n for PVA is 1.78 and for its additives film n varies from 1.60-1.65 at 305K temperature. As the temperature increases the value of k and n (for all the sample) increases upto 355K and then decreases. The k and n increases, as the number of functional groups appeared in the PVA matrix for the entire temperature range (Fig. 10 and 11).



Figure 10:- Variation of extinction coefficient (k) of PVA and doped PVA with different functional group of additives



Figure 11:- Variation of refractive index (n) of PVA and doped PVA with different functional group of additives

X-ray diffraction (XRD) studies

X-ray diffraction is an indispensable tool for identifying the nature of material: crystalline or amorphous. In an amorphous material the atom are arranged in a random way similar to the disorder we find in a liquid, while in crystalline materials the atoms have a regular periodic arrangement, which is lacking in an amorphous materials. The actual chemical entity is arranged in the lattice, which results the structure of the material.

In this chapter XRD spectra of PVA has been taken on PANalytical (X'Pert) having CuK_{α}, as radiation source of wavelength λ =1.542 Å with

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the 2θ values at the rate 2^{0} /min and the XRD spectra of PVA composite films have been recorded on Bruker (D₈ advance) having the same radiation source of wavelength λ =1.0573 Å with the 2 θ values at the rate 0.5⁰/min. The power of these XRD systems was 1800 watts and 1600 watts respectively. Figure 12 (a-e) shows the Xray diffraction pattern of pure PVA and PVA composite films. As PVA is polycrystalline in nature [28-32], the peak appeared in Figure 12(a) verified it. In the Figures 12b-12e, the appeared broad peaks are attributed to the crystalline domain of PVA and rest of the pattern of all figures show the polycrystalline nature except

MA doped film which is found amorphous

(Fig.12c).







Figure 12b:- XRD pattern of PVA film doped with Oxalic acid



Figure 12c:- XRD pattern of PVA film doped with Malic acid



Figure 12d:- XRD pattern of PVA film doped with Tartaric acid



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Differential scanning calorimetry (DSC) Studies

Figure 13a-13c shows the DSC thermograms for PVA doped with 5wt% amount of different functional group of additives. The value of T_g is calculated by half Cp extrapolated method. It is a known fact that below T_g , molecules do not have segmental motion, and some portions of the molecules may not wiggle around, but may only be able to vibrate slightly. Near T_g , the molecules can start vibrating and segmental motion increase. The conformational changes, i.e. changes in molecular shape, are caused either by thermal motion or by the action of an external field without rupture of chemical bonds.

The figure 13a-13c shows that the position of T_g for PVA films filled with different number of functional group of additives, was shifted toward lower temperature, as compared to the T_g of pure PVA films (85°C), which has already determined by Raju et al. [24]. Table 2 suggests the reduction in the thermal stability. This shows that the segmental mobility of PVA increased with the addition of more functional groups and the PVA segments became less rigid. The XRD pattern of PVA composite films are in agreement with the results emerging out of Tg. This indicate that the dopants acts as plasticizer in PVA, therefore, the molecules of the additives (having different functional groups) greatly affected the PVA structure.



Figure 13b:- DSC thermograms of PVA film doped with Malic acid A Journal for New Zealand Herpetology



4. Conclusion

- The dielectric parameters like $\epsilon', \epsilon'', \sigma, \tau, tan\delta, k and n$ depend on the number of functional groups present in the polymeric film as an additives. The existence of functional groups decreases the dielectric permittivity for entire temperature range, whereas the remaining parameters showed maxima at 355K in the investigated temperature range. The temperature dependence of ϵ' for all investigated samples is insignificant but presence of dopants in the film samples significantly affects the parameter ϵ' .
- In general, at microwave frequency the movement of network and modifying ions are held responsible for relative ε' and oscillations between them for loses. The dielectric constant (ε') at microwave frequency for doped PVA films is found in the range 2.42-2.54, which is quite lower than that of virgin PVA film 3.08, hence such films with lower ε' can be used in microelectronic applications and will give better contribution as compared to pure PVA film.
- The study of ac conductivity of the PVA and its composite films suggests that σ' increases with the increase in temperature up to 355K, on further increasing the temperature σ' shows a decreasing trend. At low temperature hydrogen bonding is stronger between PVA and its additives. Conductance will be low due to less availability of free polar centres, as temperature increases hydrogen bonding become weaker, which enhances number of free polar centres in the lattice, causing

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increase in conductance. The ac conductivity follows the Arrhanius law with activation energy in the investigated temperature range. The separate conducting phases also explain that the electrolytes have an apparently Arrhenius-like behaviour. The very low value of the activation energies indicate that the conduction mechanism may be due to electrons rather than ions.

- The XRD studies of the PVA and PVA composite films show the polycrystalline nature except PVA/MA composite film, which is found amorphous in nature.
- DSC studies of the sample under investigation have been revealed that as the presence of functional group in PVA increases, the T_g decreases. The DSC thermograms indicate only one T_g for each investigated film, which confirms that the additives are miscible in PVA matrix.
- All the results obtained from various parameters of PVA and doped PVA with functional group of additive films, clearly show that the presence of the number of functional group in the PVA lattice significantly affect the physical properties of the virgin PVA film.

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