Comparative Study of Dielectric Properties of (Ni Zn Ferrite Nanoparticles /Polypyrrole) Composites with different PPy percentages

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Abstract: Ferrite/polypyrrole composites comprise a new generation of multifunctional materials that combine the properties of conducting polymers and magnetic materials. In the present paper, nano-size particles of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ that have been prepared by co-precipitation method are thoroughly mixed with polypyrrole (PPy) with different weight ratios of the two constituents. The dielectric constant (ε'), ac conductivity (σ′) and the dielectric loss factor (tan δ) are measured for the pure Ni Zn ferrite sample, the pure polypyrrole sample and composite samples with different PPy percentages to report a comparative study of the corresponding measurements. The results of dielectric constant (ε') and dielectric loss factor (tan δ) reveal a significant difference in value between the sample of the pure ferrite and the other samples either of the PPy sample or the PPy/ferrite samples. The high values of (ε') in the PPy sample and the PPy/ferrite samples can be attributed to the strong correlation between polarization mechanism and conduction mechanism, besides they suggest also a heterogeneous structure of the polypyrrole consisting of highly conducting islands embedded in a resistive matrix so that the interfacial polarization has such a great value. The results show also that the ac conductivity (σ′) of the pure PPy sample is higher than that of the composite samples, and obviously show that (σ′) values of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ / PPy composites increases with increasing PPy content as expected and in consistence with the suggestion of the strong correlation between polarization mechanism and conduction mechanism . The present composites may be very useful in some important applications such as electromagnetic shielding.

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Key words: Ferrite/polypyrrole, composites, nano-size particles ,magnetic materials, conduction mechanism, conducting polymers , dielectric

1. Introduction

Magnetic composite materials comprise a new generation of multifunctional materials that combine the properties of polymers and magnetic materials (ferri- and/or ferromagnetic particles mixed or embedded in a matrix), that one could call magneto-polymeric materials [1]. The features of conducting polymers such as availability in film form and good environmental stability enhance their potential use in practical applications in various fields [2]. Some of these applications are electromagnetic interference shielding, rechargeable batteries, light emitting diodes, electro-catalysts, electrodes, sensors, corrosion protection coatings and microwave absorption [3,4]. Most practical polypyrroles have conductivities in the range of 1–100 S cm^{-1} [2]. Due to the relatively high conductivity in conducting polymers, eddy current losses may be encountered as a problem in some applications. However, ferrite particles have an advantage of reducing the eddy current losses due to their high electrical resistance [5]. Moreover, the electromagnetic properties of ferrites can be tailored by controlling the different types and amount of metal ions substitution [6]. Finally, it is worth noting that although the electrochemical polymerization of pyrrole has been extensively studied as it is easily obtained in the form of freestanding films [2], the advantage of chemical polymerization is the possibility to obtain bulk quantities of magneto-polymeric materials for industrial applications [1]. Further development of synthetic methods to produce novel electrical-magnetic composites with well designed structure, relatively good magnetic and conductive properties is highly desirable [7].

2. Experimental procedure

2.1. Preparation

The starting materials are nano-structured particles of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ which were previously prepared by chemical co-precipitation (details of preparation, XRD and IR spectra are published [8]) and polypyrrole prepared by chemical polymerization using anhydrous ferric chloride as an oxidizing agent. The studied samples are formed by thoroughly mixing PPy and ferrite powders with weight percentages of PPy = 100%, 80%, 60%, 40%, 20% and 0.0%.

2.2. A.C. measurements

The dielectric constant (ε'), ac conductivity (σ'_{ac}) and dielectric loss factor (tan δ) have been measured by a complex impedance technique using a lock-in amplifier,(Model SR 510 Stanford Research

Systems) as functions of frequency in the frequency range 10-10^5 Hz at different temperatures. The powder samples were pressed into a cylindrical cell, which has two metal electrodes connected to the circuit shown in Fig. (1). An ac voltage (V) with frequency (f) is applied to the sample. A small resistor (R) is connected in series with the sample. The current is given by ($I_R = V_R/R$) where (V_R) is the drop voltage on (R). The lock-in amplifier is used to measure simultaneously the voltage (V_R), the frequency of the applied voltage (f) and the phase difference (φ) between the applied ac voltage (V) and (V_R). The dielectric constant is calculated by: $\varepsilon' = (11.3\times10^{12}\, d\, V_R \sin\varphi) / R\,\omega\, A$, the real part of ac conductivity is given by $\sigma' = (V_R\, d \cos\varphi) / R\, A$, and the dielectric loss factor is given by $\tan\delta = 1/\tan\varphi$; where d is the thickness of the sample in cm and A is the area of the disc shaped surface of the sample in cm^2.

3. Results and Discussions

Fig. (2) (a-f) shows the frequency dependence of the dielectric constant (ε') at different temperatures for all investigated samples. In the Ni Zn ferrite sample (Fig.2-a), the phenomenon of dielectric dispersion can be explained – as usual - on the basis of Maxwell–Wagner model and Koop's phenomenological theory [9] of dielectrics. In this model, a dielectric medium has been assumed to be made of well conducting grains, which are separated by poorly conducting grain boundaries. At lower frequencies, the grain boundaries are more effective than grains in electrical conduction [10]. The higher values of the dielectric constant observed at lower frequencies are because of accumulation of charges at the boundaries, pores and defects under the influence of electric field, causing an appreciable interfacial polarization [11]. In ferrites, there is a strong correlation between the conduction mechanism and the dielectric behavior, in other words the mechanism of the polarization process in ferrites is similar to that of the conduction process where it is observed that the electronic exchange between $Fe^{2+}\leftrightarrow Fe^{3+}$ results in local displacements which determine the polarization [12] and simultaneously the conduction. The decrease of dielectric constant with increasing frequency is expected since the main contributor to the value of the dielectric constant in ferrites (the interfacial polarization) cannot follow the alternation of the electric field when the frequency increases. On the other hand, in PPy (Fig. 2-b), it is observed that for the PPy sample ε' has essentially higher values especially at low frequencies, which are also attributed to an interfacial polarization in the polymer caused by the dispersion of islands of conductive regions into the system [13]. Also, in general, it is assumed that the charge carriers move by hopping between pairs of sites oriented at random with respect to the applied field [14] and like the case of ferrites the observed rapid decrease in (ε') is expected with increasing frequency as the predominant contributor to the polarization – i.e. the interfacial polarization- can no longer follow the variation of the field. In spite of this similarity in mechanisms, considering Fig (2- a, b), it can be obviously seen that (ε') values of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrite sample are lower than those of the polypyrrole sample which is confirmed by Fig. (3) where (ε') values of the composites with different PPy percentages at a chosen frequency are displayed. It is seen that (ε') increases with increasing PPy content. The interpretation of those higher values may be due to the much higher conductivity of the conductive regions in PPy than the corresponding conductive regions in ferrite leading to the accumulation of greater numbers of charge carriers at the boundaries in PPy than the corresponding ones in ferrite.

The temperature dependence of (ε') in the six samples is as expected i.e. increasing by increasing temperature due to the above-mentioned correlation between the dielectric constant and conduction mechanism and by considering the semiconducting nature of ferrites, [15] and the temperature activated conduction in polymers [13].

Fig. (4) displays the frequency dependence of the real part of ac conductivity at different temperatures. It is noticed that, in most of the samples, in the frequency range (10^3 to 10 Hz), we can observe that σ′(f) is almost independent of frequency and its value is approximately equal to the dc conductivity. At higher frequencies, there is an increase in σ′(f) and the samples seem to obey the relation [16]:

$$\sigma'(f) = \sigma_{DC} + \sigma(f)$$

The first term (σ_{DC}) is frequency independent and is given by the Arrhenius relation:
$\sigma_{DC} = A \exp[-E/kT]$. The second term (σ (f)) is related to the dielectric relaxation caused by bound charge carriers, which depends on frequency [17]. It is mentioned above that the hopping of charge carriers is usually considered as the main contributor to the conduction process in either ferrite or polypyrrole, so the increase in conductivity with increasing frequency does not mean that the number of charge carriers increases, but only the rate of hopping of charge carriers increases, resulting in increase of conductivity and decrease of resistivity [18]. The second term also can be written in the form ($\sigma(\omega) = a\omega^n$), where $\omega = 2\pi f$ and the exponent n defines the frequency dependence, its value often falls in the range ($0 < n < 1$). Moreover it is observed that the conductivity of the pure PPy sample is higher than the composite samples and that the ac conductivity values of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ / PPy composites increases with increasing PPy content, which is in consistency with all the above discussion and is confirmed by Fig. (5)

where (σ') values of the composites with different PPy percentages at a chosen frequency are displayed.

Fig. (6) shows the frequency dependence of the dielectric loss factor (tan δ) at different temperatures where it is shown that tan δ decreases with increasing frequency at lower temperatures, this dispersion is exhibited due to the Maxwell–Wagner two-layer model interfacial polarization and in agreement with Koops' theory too [19]. However, at higher temperatures, there are some few peaks. Generally, a maximum in tan versus frequency appears when the frequency of the hopping charge carriers coincides with the frequency of the applied alternating field [12]. A broad peak of dielectric loss tangent (tanδ) indicates the existence of a distribution of relaxation times rather than a single relaxation time. This distribution of relaxation times is generally attributed to the difference in the environment surrounding different charge carriers in the materials, in addition, the interactions between charge carriers and thermal fluctuations of the lattice are not identical every where and at every time [20].

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4. Conclusion

The results of dielectric constant (ε') and dielectric loss factor (tan δ) reveal a significant difference in value between the sample of pure ferrite and the other samples either of the PPy sample or the PPy/ferrite samples.

The high values of (ε') in PPy sample and PPy/ferrite samples can be attributed to the strong correlation between polarization mechanism and conduction mechanism, besides they suggest also a heterogeneous structure of the polypyrrole consisting of highly conducting islands embedded in a resistive matrix so that the interfacial polarization has such a great value. The results show also an observable dependence of (ε') and (tan δ) on the weight percentage of PPy/ferrite. Also, it is found that the conductivity of the pure PPy sample is higher than the composite samples and that the ac conductivity values of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ / PPy composites increases with increasing PPy content. Due to this relatively high conductivity in conducting polypyrrole, eddy current losses may be encountered as a problem in some applications. However, mixing PPy with ferrite particles with calculated percentages may have the advantage of reducing the eddy current losses in relatively high frequency applications. The present composites may also be very useful in electromagnetic shielding because of combining the shielding effect of the "conducting" polypyrrole to that of the "magnetic" ferrite.

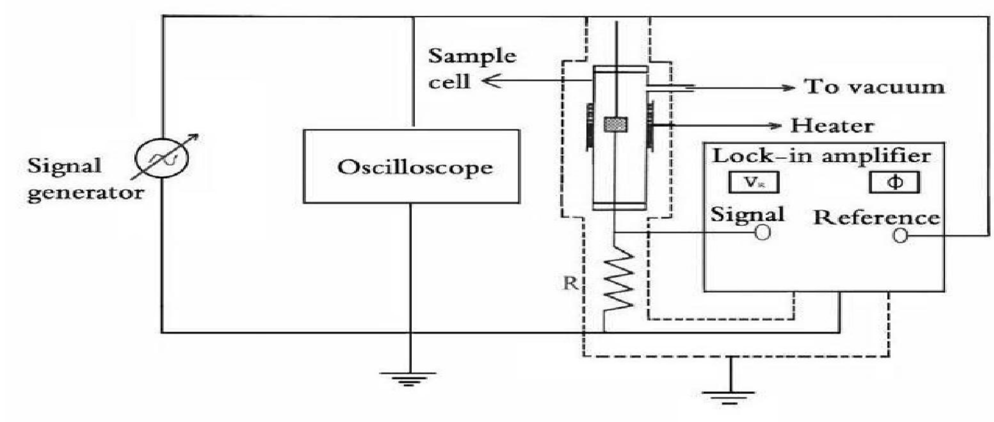

Fig. (1) Block diagram of the experimental arrangement for measuring A.C. Properties by using a lock-in amplifier.

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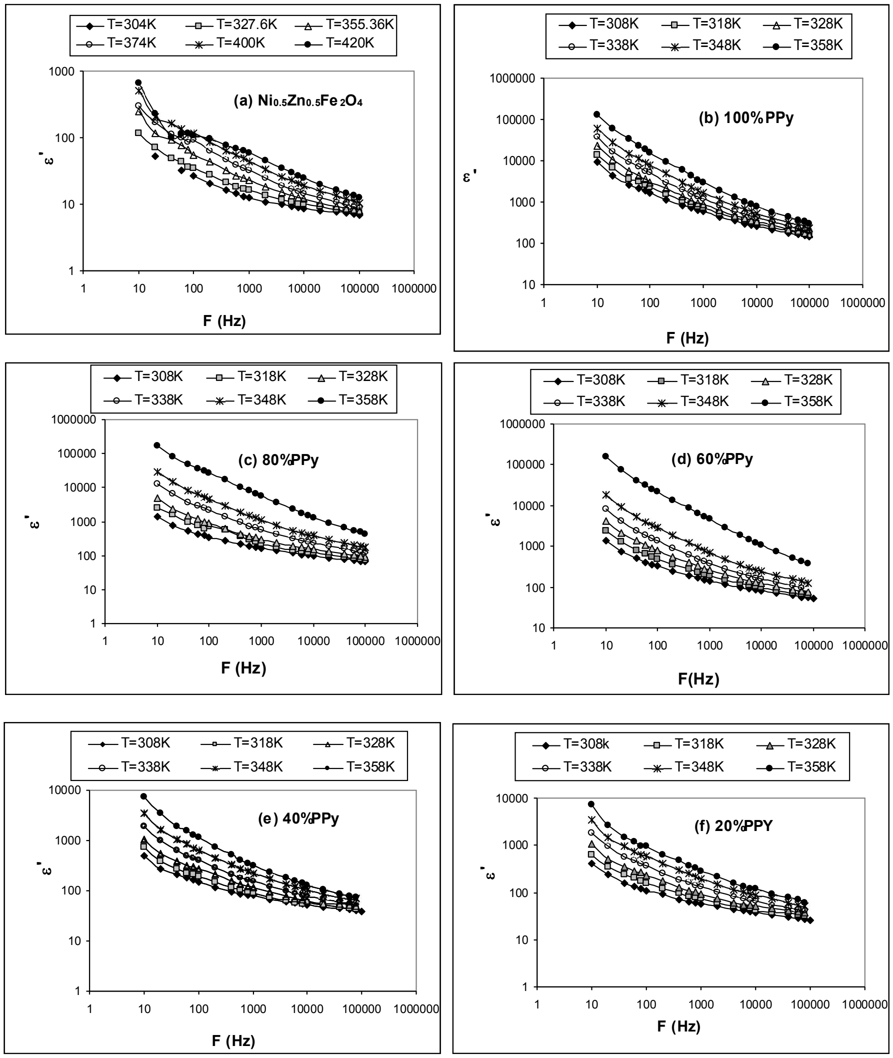

Fig. (2) Dielectric constant (ε') *vs.* frequency for PPy-$Ni_{0.5}Zn_{0.5}Fe_2O_4$ composite samples with different PPy content at different temperatures.

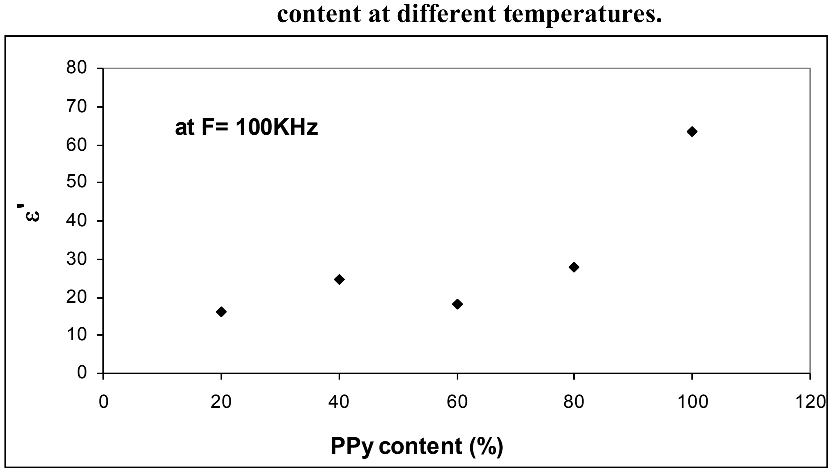

Fig. (3)

Fig. (3) Dielectric constant (ε') values of the composites with different PPy percentages at a chosen frequency are displayed.

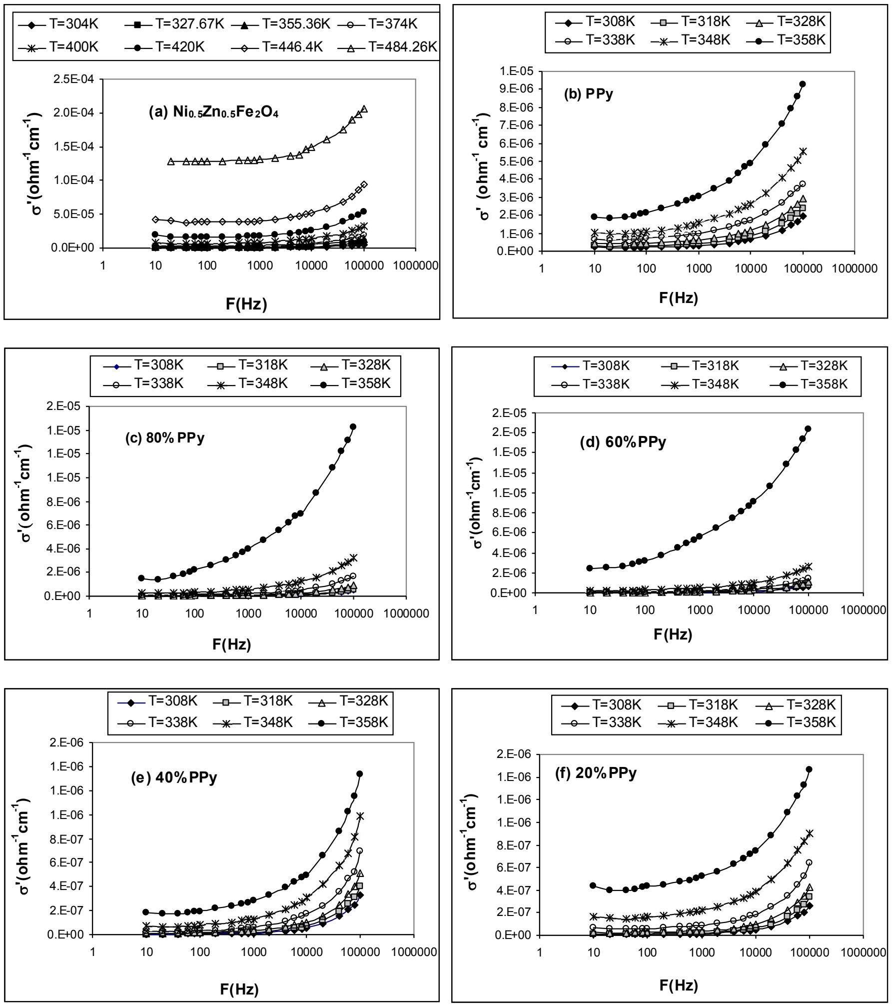

Fig. (4) A.C. conductivity (σ') *vs.* frequency for PPy-$Ni_{0.5}Zn_{0.5}Fe_2O_4$ composite samples with different PPy content, at different temperatures.

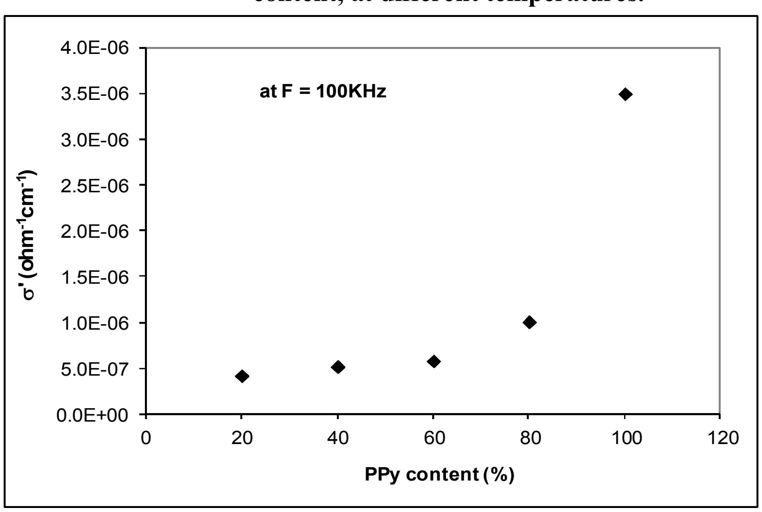

Fig. (5) A.C. conductivity (σ') values of the composites with different PPy percentages at a chosen frequency are displayed.

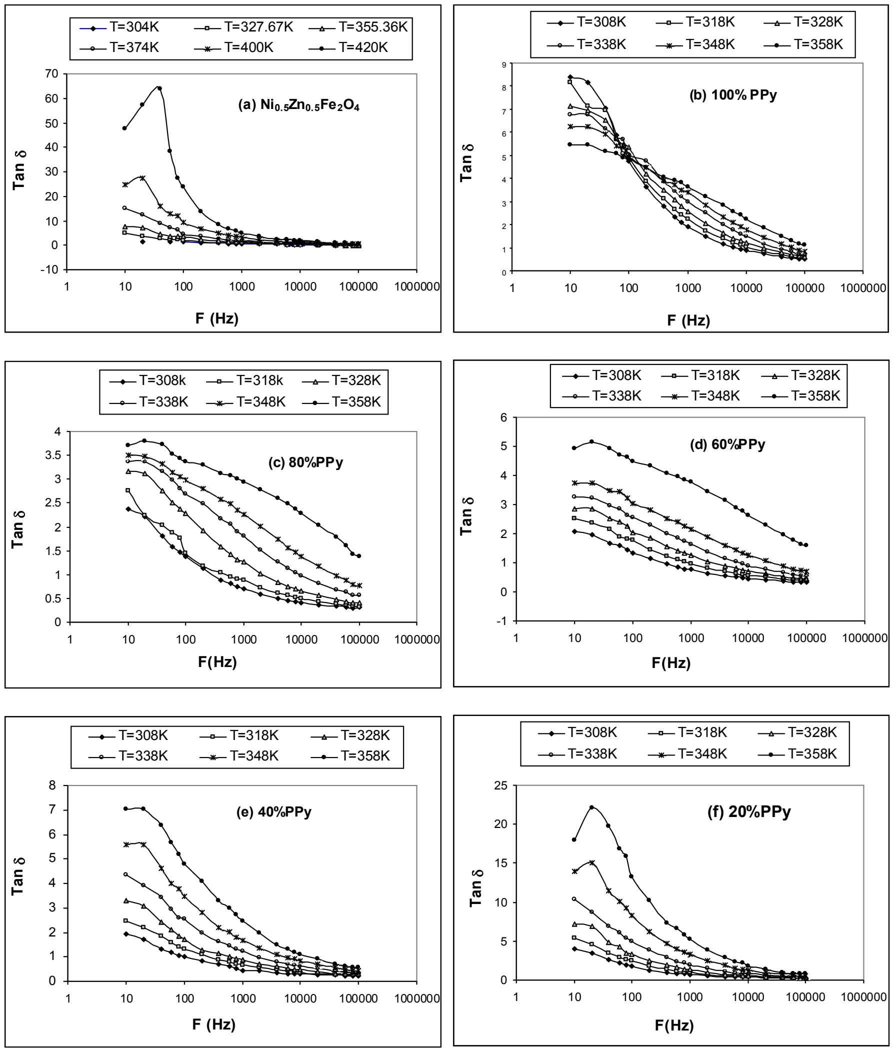

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Fig.(6) Tan δ *vs.* frequency for PPy-$Ni_{0.5}Zn_{0.5}Fe_2O_4$ composite samples with different PPy content at different temperatures.

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