

Development of nickel modified Fe₃O₄ solar selective coatings for solar absorber applications

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Abstract

We report the development of Fe₃O₄/Cu, and Ni-Fe₃O₄/Cu based spectrally selective coatings for solar absorber applications using two different electrochemical baths. The deposition processes were optimized for both electrochemical baths and it was observed that the controlled introduction of nickel in Fe₃O₄ matrix is important to achieve enhanced solar thermal response. The fabricated coatings were characterized to understand the structural, micro-structural and optical properties, to investigate their phase, chemical composition, surface morphology, thickness and solar thermal properties. Ni-Fe₃O₄ composite coatings exhibited improved adhesion to Cu substrate and allowed better thickness control when compared to Fe₃O₄ structures without Ni. Improved substrate adhesion and optimized thickness resulted in better optical properties for these coatings. The optimized Ni-Fe₃O₄ coatings exhibit maximum spectrally averaged absorptivity ($\alpha = 0.87$) in the 300 – 900 nm wavelength range, and minimum spectrally averaged emissivity ($\varepsilon = 0.18$) in the 2.5 – 25 μm infrared range at room temperature. For Fe₃O₄ coatings developed on Cu substrates without Ni, maximum absorptance and minimum emittance values obtained were 0.76 and 0.08 respectively. Ni-Fe₃O₄ coating thickness was measured $\sim 32 \mu\text{m}$. Copyright © 2016 VBRI Press

Keywords: Solar selective coatings, electrochemical deposition, absorptance, emittance, copper substrate.

Introduction

The application of solar energy is important to reduce the dependency on non-renewable energy sources such as fossil fuels, which are depleting with time and also have severe impacts on environment. In contrast, solar energy is considered clean and is in abundance, yet there is a need to devise novel ways to harness solar energy for possible applications, such as domestic water heating, industrial process heating or solar electricity generation [1]. The key requirement for such applications is the conversion of solar energy into thermal energy or electrical energy. The direct conversion of solar energy into electricity relies on photovoltaic devices, whereas thermal energy conversion relies on efficient collection of solar energy and its conversion into thermal energy. The later can be achieved by using spectrally selective coatings on solar collectors, also called receivers. These spectrally selective coatings should act as an ideal absorber in the solar spectral range and

reflector in the infrared spectral region to achieve the best solar thermal response [2]. In addition to the high absorptance and low emittance, the spectrally selective coating materials should be easily available, having low synthesis cost and long term stability under operating conditions and should also be eco-friendly. Several coating fabrication techniques are in practice, e.g., chemical vapor deposition (CVD) [3-5], physical vapor deposition (PVD) [6 - 8], spray [9, 10], sol-gel [11-13] and electrochemical [14, 15] etc. Among these available techniques, electrochemical or electroplating technique is attractive, due to its low synthesis cost, simple operational procedures and large surface area coating capability [14]. Black Ni was among the first coatings developed for solar absorber applications. H. Tabor [16] is known for the first contribution on the development of black Ni solar absorber coating in the United States in the 1950s. Tabor's black Ni is described as a complex of Ni-Zn-S system. Cantu et

al. [14] developed black Ni solar selective coatings on stainless steel substrates using the electrochemical technique. A silica based sol-gel antireflection coating was also applied on top. The developed coatings have a maximum solar absorptance ~ 0.91 and minimum thermal emittance ~ 0.1 . Similar black Ni coatings have been reported by Voinea et al. [15] on Cu substrates. Although, black Ni coatings were reported with high absorptance and low emittance for solar absorber applications, these structures usually degrade in humid environments [16]. One of the most widely explored solar selective coating material is the electroplated black chrome, mainly due to its high absorptance, optimum stability under wide range of oxidation-reduction environments along with high thermal resistance upto 300 °C [18, 19]. The first systematic synthesis of black chrome electrochemical coatings was reported by McDonald [20]. Bayati et al. [18], fabricated black chrome coatings on Cu substrates having high absorption ~ 0.96 . However, one disadvantage of black chrome is its chromium (+6) content in electrochemical baths, which is toxic and harmful to the environment. Even when working with Cr (+3) ions in electrochemical baths, the presence of Cr (+6) in the electrolyte and the coatings developed using the bath due to redox reactions cannot be overruled, indicating the inherent toxicity issues associated with the utilization of Cr (+6) for fabricating solar selective coatings. For example, the toxicity of Cr has been defined by the Environmental Protection Agency (EPA), USA standards, where the allowed Cr in drinking water is 100 ppb [21].

Iron oxide, usually called black iron, is another material which has better durability than black Ni under humid atmospheric conditions [22] and is also non-toxic. However, it was reported to have lower absorptance ($\alpha = 0.85$) [22]. The minimum thermal emittance for this coating was reported to be 0.1. The reason for low α has been attributed to the high refractive index of iron oxides ($n(\text{Fe}_3\text{O}_4) \sim 2.42$, $n(\text{FeO}) \sim 3.32$), leading to large reflection losses from the surface [23]. In this work, we have considered Ni modified Fe_3O_4 composite, Ni- Fe_3O_4 , coatings as an alternative to black Ni and black chrome spectrally selective coatings, mainly to take advantage of good adhesive characteristics of Ni coatings on Cu substrate and low cost, non-toxic & better durability properties of iron oxide. Also a slightly lower refractive index of Ni ($n(\text{Ni}) \sim 1.9$) [24] than iron oxide is expected to marginally improve the absorbance characteristics of the Ni- Fe_3O_4 composites. Fe_3O_4 coatings without Ni were prepared for comparison purposes. Fabrication of both the coatings on Cu substrate - (a) iron oxide without Ni ($\text{Fe}_3\text{O}_4/\text{Cu}$) and (b) iron oxide with Ni (Ni- $\text{Fe}_3\text{O}_4/\text{Cu}$) were achieved using the electrochemical deposition technique. Besides solar absorber application of black iron mentioned above, electrochemical Fe_3O_4 coatings on various substrates [18, 25, 26] and Ni-Fe composite coatings [27, 28] have been reported,

which were characterized for their magnetic properties. The spectral selective properties of Ni modified iron-oxide composite materials are not available. Electrochemical deposition of iron has frequently been facilitated by the use of a complexing agent. Kothari and co-workers [26] reported the use of tri-ethanolamine (TEA) chemical to deposit Fe_3O_4 films in alkaline medium. Horkans [29] studied the effect of boric acid on the electrodeposition of NiFe alloys. We report the development and optimization of nickel iron-oxide composite coatings using boric acid. Iron oxide based coatings are important because they are in-expensive, non-toxic, easily available and have low fabrication cost. Although, development of iron oxide based coatings for solar absorber applications have been reported, the reports are few and characterizations of the properties are not exhaustive. In this paper, we have investigated issues regarding deposition of iron oxide based coatings on Cu and evaluated the optical performance of nickel modified iron oxide.

Experimental

Materials

The following chemicals were used in the experiment: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Fisher, 97%), $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (Sigma), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Fisher, 97%), H_3BO_3 (Fisher, 99.5%). Cu and SS sheets were bought locally.

Fabrication of iron oxide ' Fe_3O_4 ' on copper 'Cu' substrates

Commercially available 0.4 mm thick Cu sheets were cut into rectangular 3 cm \times 2 cm pieces as substrates for electrochemical deposition of iron oxide coatings. These substrate pieces were subjected to various cleaning treatments. Initially, they were ground and polished with 1000 Grit sand paper to remove surface defects, especially oxide layers on the surface, if any. The ground substrates were then cleaned with lime and salt, followed by washing with soap solution and distilled (DI) water. Subsequently, they were dried using a hot air drier. These dried substrates were treated in hot solution ~ 80 °C of trichloroethylene and acetone respectively for 5 minutes to get rid of any residual oil contaminants during the cleaning process. Finally, copper substrates were heated at 120 °C for 3 hours. These thermally treated cleaned substrates were used for electrochemical deposition in electrochemical bath under two electrode conditions. The electrochemical bath was prepared by dissolving 0.08g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 98%) in 200 ml DI water and stirred for an hour to homogenize the solution. The substrates were used as working electrode and a platinum 'Pt' rod was used as the counter electrode. The deposition process was optimized by varying surface current density in the range 0.03 – 0.08 A/cm² for different time intervals in the range of 5 – 15 minutes. The deposited iron

oxide films were dried in an oven at 100 °C for 3 hours for further characterization. The optimized iron oxide thin films exhibited absorbance and emittance $\sim 0.7 \pm 0.04$ and 0.08 ± 0.04 respectively. The pristine iron oxide films are limited with lower absorbance, even though films showed good emittance values.

Fabrication of Ni-Fe₃O₄ on copper 'Cu' substrates

The chemical composition of the iron oxide bath was modified by adding extra nickel. The modified electrolyte bath was prepared by mixing 40g NiSO₄.6H₂O, 10g Fe₂O₁₂S₃.xH₂O, 12g NiCl₂.6H₂O and 8g H₃BO₃ in 200 ml DI water contained in a 600 ml beaker. The solution was stirred continuously using a magnetic stirrer for 3 hours till a complete transparent greenish homogeneous solution was obtained. This electrolyte bath was used with a 3 cm x 2 cm substrate 'Cu' as the working electrode, and antimony selenide 'SbSe' as a counter electrode to deposit nickel modified iron oxide 'Ni-Fe₃O₄' composite coatings. The substrates were coated by varying surface current density in the range of 0.17 – 0.20 A/cm² for various time intervals within 30 – 120 seconds. The as prepared thin films were subjected to ultrasonic cleaning for 1- 2 minutes, followed by nitrogen drying to remove any residual surface debris. The nitrogen dried films were finally dried at 120 °C for 3 hours in an oven. These coatings showed good adhesive properties, better absorbance, $\alpha \sim 0.9 \pm 0.05$ and low emittance, $\varepsilon \sim 0.18 \pm 0.04$. The optimization of electrolytic deposition is still going on to improve optical properties of nickel modified iron oxide composite ceramic layers to realize better solar thermal performance.

Characterization of the Fe₃O₄/Cu, and Ni-Fe₃O₄/Cu films

X- Ray Diffraction (XRD): X-ray diffraction patterns of electrodeposited iron oxide and nickel modified iron oxide coatings were recorded using a Bruker D8 ADVANCE instrument at 40KV and 40 mA in the Locked Couple mode, using Cu K α radiation ($\lambda = 1.54056\text{\AA}$) and scanned at a rate of 0.02° per sec over a range of 20° < 2 θ < 80°.

Scanning Electron Microscopy (SEM) measurements: SEM, ZEISS EVO 18 was used to determine the surface morphology of these electrodeposited iron oxide and nickel modified iron oxide coatings. The Ni-Fe₃O₄/Cu films were mounted on SEM stubs and scanned over the surface. The higher magnification was used to understand the surface morphology and low magnification was used to record energy dispersive X-ray (EDX) spectrum to understand the compositional distribution of elements.

UV-Vis spectroscopic measurements: The ability of these coatings to absorb sunlight in the UV-Vis

spectral regime was investigated using Cary 4000 Spectrophotometer using the Diffuse Reflectance Accessory (DRA) attachment, in the 300 – 900 nm wavelength range. From the reflectance data, spectral absorbance was calculated using $\alpha(\lambda) = 1 - R(\lambda)$, for opaque samples, and solar absorbance α_s was determined from the formula given below, where I_s is the solar energy spectral distribution (reference spectrum: AM1.5 Global) [30].

$$\alpha_s = \frac{\int_{0.3}^{0.9} I_s(\lambda)(1 - R(\lambda))d\lambda}{\int_{0.3}^{0.9} I_s(\lambda)d\lambda}$$

Fourier Transform Infra-Red (FTIR) spectroscopic measurements: The room temperature emissive properties of the films were characterized using Bruker Vertex 70v Fourier Transform Infrared Spectroscopy (FTIR) instrument. The reflectance spectrum was recorded in the IR wavelength range of 2.5 μ m to 25 μ m for all the fabricated coatings and used to calculate the emissivity of these films using the formula [31]:

$$\varepsilon_t = \frac{\int_{2.5}^{25} (1 - R(\lambda))E_b(\lambda)d\lambda}{\int_{2.5}^{25} E_b(\lambda)d\lambda}$$

where, $I_s(\lambda)$ is the solar spectral radiation of AM 1.5 according to the ISO standard 9845-1 (1992), $R(\lambda)$ is the measured reflectance at a specific wavelength λ and $E_b(\lambda)$ is the blackbody spectral radiation. The temperature, $T = 373$ K was used for calculating ε_t .

Results and discussion

The initial experiments were carried out using first electrochemical bath containing only FeCl₂.4H₂O as an iron source, in DI water solution. The resulted Fe₃O₄ on copper substrate showed the maximum absorbance ($\alpha = 0.76$) and minimum emittance (0.07). These values were reasonable but the process didn't offer control on coating thickness and the adhesive properties of the films were not optimum, once thicknesses of these coatings were increased. The poor adhesive properties with increasing coating thickness restricted maximum absorbance α to ~ 0.76 and it was not possible to further improve α with this electrolyte bath. The need to improve adhesive characteristics as well as overall absorbance necessitated the exploration of alternative electrolyte baths, where better results may be achieved. Nickel coatings on Cu substrates [32] had been previously developed and show good adhesive property. To improve the adhesive and absorbance properties, coatings on Cu, Ni modified iron-oxide coatings were developed. The modified electrolyte bath was made of NiSO₄.6H₂O, Fe₂O₁₂S₃.xH₂O, NiCl₂.6H₂O and H₃BO₃. Additional nickel precursors in conjunction with boric acid produced coatings with better adhesive properties,

subsequently enhancing solar thermal performance. The XRD patterns of these nickel modified iron oxide composite coatings are shown in **Fig. 1**. In conjunction with copper substrate peaks, metallic nickel, iron with some nickel iron and nickel sulfur contents are identified and indexed in **Fig. 1**.

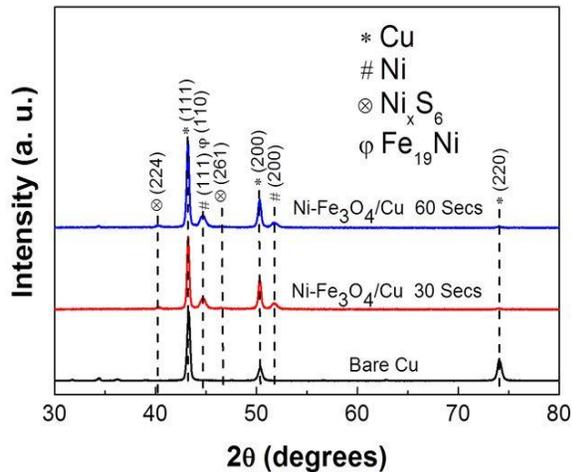


Fig. 1. XRD patterns for Ni-Fe₃O₄/Cu films (60 and 30 seconds) along with Bare Cu.

Although, Ni and Fe oxide peaks were expected, they were not observed, suggesting the amorphous nature of the oxide phases in these coatings. SEM characterizations were performed to understand the surface properties and their effect on solar thermal performance, especially on emissivity, which greatly relies on surface roughness. The recorded SEM images of the Ni-Fe₃O₄/Cu coatings deposited for 60 seconds and 30 seconds are shown in **Fig. 2(a)** and **2(b)** respectively. The grinding/polishing imprints of the Cu substrates, generated during cleaning process, are observed for both coating structures deposited for 60 and 30 seconds, as shown in **Fig. 2(a)** and **(b)**. To understand the surface morphology, we also carried out SEM measurements on bare copper substrate and results are shown as an inset in **Fig. 2(a)**. These characterizations clearly suggest that the substrate surface roughness greatly affects the coating roughness. Thus roughness of the substrate should be minimized to achieve coatings with smoother surfaces, and lower emissivity values. The surface morphology of Ni-Fe₃O₄/Cu thin film depicts the granular growth of nickel modified iron oxide thin films. We propose that substrate rough imprints are acting as the nucleation center, promoting growth along these directions, and thus, leaving substrate imprints on the top surface of these deposited structures. The cross-sectional SEM micrograph of these coatings obtained after 30 second of electrodeposition, is shown in the inset of **Fig. 2(b)**. The interface between Cu-substrate and the Ni-Fe₃O₄ coating could be clearly identified and has been marked using two white arrows for clarity. The thicknesses of the Cu substrate and the deposited

coating were measured through this cross sectional microscopic measurement and were found to be ~322 μm and 34 μm, respectively. The original thickness of the Cu-substrate was 0.4 mm and the difference observed in SEM image is attributed to the material loss during grinding/polishing of the substrate prior to electrochemical coating. The elemental chemical compositions for these films were estimated using EDX, and their measured EDX spectra with respective atomic fractions are listed in **Fig. 2**.

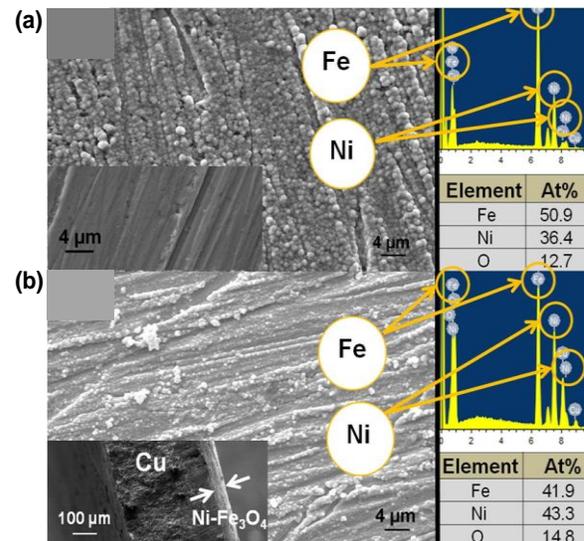


Fig. 2. SEM images and corresponding EDX analysis of Ni-Fe₃O₄/Cu film deposited using 0.17 A/cm² for (a) 60 seconds and (b) 30 seconds along with the corresponding EDX studies of chemical compositions. Inset of 2 (a) shows the surface of Bare Cu. Inset of 2(b) shows the cross-section of 30 seconds Ni-Fe₃O₄/Cu film. Film thickness of Cu and Ni-Fe₃O₄ were measured to be 322 μm and 34 μm respectively.

We clearly observed Ni and Fe peaks in these EDX spectrum and atomic fraction for Fe, Ni and O are 50.9, 36.4, and 12.7% for coating obtained after 60 seconds of electrodeposition, **Fig. 2(a)** and are 41.9, 43.3 and 14.8% for 30 second deposited one, **Fig. 2(b)**. The measurements suggest that nickel modified films are rich in metallic content, a favorable condition for high absorptance and low emittance for these fabricated structures. In addition, the observation of low atomic fraction of oxygen, also substantiate the absence of oxide peaks in XRD measurements, suggesting, the presence of either in amorphous or smaller fraction, not detectable within the XRD limits. The optical reflectance of these fabricated structures was carried out to understand their solar thermal performance, especially the absorptance and emittance in the desired wavelength range. The reflectance measurements were carried out in diffuse reflectance conditions within 300 – 900 nm wavelength range and used to calculate the absorbance for these structures. The measured absorbance results are summarized in **Fig. 3(a)**, together with bare copper substrates. These

measurements were also used to calculate the total absorptance and the measured values are listed with respective absorbance curves. We observed that absorptance values are $0.85 \pm 0.04 < \alpha < 0.87 \pm 0.04$ for these nickel modified iron oxide coated structures. To understand the room temperature thermal emittance, we carried out reflectance measurements in $2.5 \mu\text{m} - 25 \mu\text{m}$ infrared region and are plotted in Fig. 3(b).

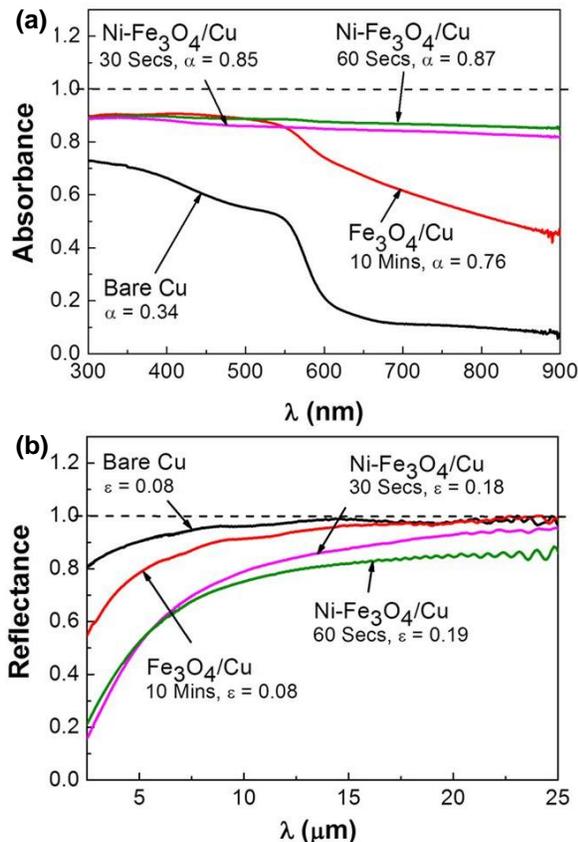


Fig. 3. (a) Absorbance and (b) FTIR - Reflectance plots for $\text{Ni-Fe}_3\text{O}_4/\text{Cu}$ films deposited using electrochemical technique. $\text{Fe}_3\text{O}_4/\text{Cu}$ and $\text{Fe}_3\text{O}_4/\text{SS}$ films were deposited using current densities in the range of $0.03 - 0.08 \text{ A/cm}^2$, while for $\text{Ni-Fe}_3\text{O}_4/\text{Cu}$ films, current densities varying within $0.17 - 0.20 \text{ A/cm}^2$ were used.

These data were used in the calculation of emittance values; the minimum was found to be 0.18 ± 0.04 for investigated structures. The $\alpha \sim 0.87$ for $\text{Ni-Fe}_3\text{O}_4/\text{Cu}$ coatings, fabricated using boric acid bath, are higher than $\text{Fe}_3\text{O}_4/\text{Cu}$ films $0.5 < \alpha < 0.7$ without the nickel and boric acid bath. This is attributed to the better adhesive property, and higher density of the films produced using the boric acid containing bath, compared to those obtained from bath without boric acid. The ε values of the $\text{Fe}_3\text{O}_4/\text{Cu}$ coatings obtained without boric acid bath were, however, in the range of $0.07-0.08$, because of lower thickness of the deposited film structures. The relatively higher ε values for the $\text{Ni-Fe}_3\text{O}_4/\text{Cu}$ are due to the relatively higher thickness and larger surface roughness. Further optimization in thickness and

substrate surface roughness may lead to the lower emissivity without affecting the absorption values for these structures. The absorptance ($0.85 \pm 0.04 < \alpha < 0.87 \pm 0.04$) and emittance (0.18 ± 0.04) values obtained for $\text{Ni-Fe}_3\text{O}_4/\text{Cu}$ coatings are similar to those reported by Mar et al.²². The $\text{Ni-Fe}_3\text{O}_4$ composition provided good quality films with better adhesive properties. Although, the absorptance values obtained for this system were lower than desired, these values can be improved by modifying the chemical composition of the coatings. As explained earlier, changing Ni:Fe content is expected to change the refractive index of the $\text{Ni-Fe}_3\text{O}_4$ composite coating, thus allowing modification of absorptance characteristics.

Conclusion

$\text{Fe}_3\text{O}_4/\text{Cu}$, and $\text{Ni-Fe}_3\text{O}_4/\text{Cu}$ solar selective coatings were developed successfully using two different electrochemical baths, one using only $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, while the other using Ni and Fe salts along with boric acid. The former electrolytic bath produced coatings with desirable ε in the $0.07-0.08$ range, but with poor spectrally selective absorption and poor control on coating thickness. On the other hand, the later electrolytic bath produced good quality, dense coatings with better adhesive properties exhibiting $0.85 \pm 0.04 < \alpha < 0.87 \pm 0.04$ and $\varepsilon \sim 0.18 \pm 0.04$. The later electrolyte bath also offers better control on coating thickness. XRD and EDX analyses of the $\text{Ni-Fe}_3\text{O}_4$ coatings confirmed metal rich oxide composite structures. These preliminary results suggest the potential of $\text{Ni-Fe}_3\text{O}_4$ as future spectrally selective coatings. Further optimization of substrate roughness and coating composition are expected to improve coating emissivity and absorptivity.

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