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Araştırma / Research

SYNTHESIS OF COPPER OXIDE (CuO) FROM THERMAL DECOMPOSITION OF COPPER ACETATE MONOHYDRATE ($Cu(CH_3COO)_2.H_2O$)

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ABSTRACT

The synthesis of copper oxide (CuO) via the thermal decomposition of copper (II) acetate monohydrate ($Cu(CH_3COO)_2.H_2O$) in air atmosphere was investigated at TG-DTG/DSC apparatus with the heating rate of 10°C min^{-1} under non-isothermal conditions from 25 to 900°C. It was seen from TG-DTG/DSC analyzes that the thermal decomposition process consists of three main steps (two mass-loss regions and a tiny mass-gain region). The obtained products at 200, 300, 400°C temperatures were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Energy disperse spectroscopy (EDS) analysis. The XRD results show that the CuO nanoparticles having the monoclinic crystal structure. The SEM images showed that CuO nanoparticles were spherical in shape. The size of CuO nanoparticles decreased with an increase in annealing temperature.

Keywords: Copper acetate monohydrate, copper oxide, thermal decomposition

BAKIR ASETAT MONOHİDRATIN ($Cu(CH_3COO)_2.H_2O$) TERMAL BOZUNMASINDAN BAKIR OKSİT (CuO) SENTEZİ

ÖZ

Bakır asetat monohidratın ($Cu(CH_3COO)_2.H_2O$) termal bozunma yolu ile bakır oksit (CuO) sentezi hava ortamında izotermal olmayan şartlar altında 10°C dak^{-1}'lik ısıtma hızıyla TG-DTG/DSC cihazında incelendi. 25°C'den 900°C'ye kadar termal bozunma prosesinin üç adımda gerçekleştiği görüldü (iki kütle kayıp bölgesi ve bir küçük kütle kazanç bölgesi). 200, 300, 400°C sıcaklıklarda elde edilen ürünler X-ışını kırınımı (XRD), Fourier dönüşümü kızılötesi spektroskopisi (FTIR), Taramalı elektron mikroskobu (SEM), ve Enerji dağıtıcı spektroskopisi (EDS) analizleri ile karakterize edildi. XRD sonuçları CuO nanopartiküllerin monoklinik kristal yapıya sahip olduğunu göstermektedir. SEM görüntüleri CuO nanopartiküllerinin şekil olarak küresel olduğunu göstermektedir. CuO nanopartiküllerin boyutu, tavlama sıcaklığındaki bir artışla azaldı.

Anahtar kelimeler: Bakır asetat monohidrat, bakır oksit, termal bozunma

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1. INTRODUCTION

In recent time, it is fairly common to perform the synthesis of the metal oxides such as copper oxide, zinc oxide due to their electronical, optical and catalytic features [1].
Metal oxides are often be preferred at the surface coatings, the production of microelectronic circuits, sensors, piezoelectric devices, and fuel cells. In addition, most of the catalysts used for the industrial operations contain an oxide as active phase, promoter or support [2]. Copper oxide (CuO) that is very important oxide has narrow band gap of 1.2 to 1.5 eV and used as a p-type semiconductor material [2-3]. CuO nanoparticles have been widely studied in the literature and has the potential applications, such as gas sensors, Li-ion batteries, semiconductors, catalysis and field emission [FE] emitters, etc. [4-9]. CuO can be obtained by using different methods such as the chemical vapor deposition (CVD), sol-gel, co-precipitation, micro emulsion, hydrothermal and spray pyrolysis [10-16]. On the other hand, all the methods include a certainly controlled synthesis environment and expensive equipment [17-21]. CuO nanoparticles can be obtained from the thermal decomposition of some copper compounds [22-23].

The aim of this paper is to develop a simple, lower cost, and rapid synthesis method to obtain high-purity CuO nanoparticles via thermal decomposition of copper acetate monohydrate. Then, the characterizations of products obtained from the thermal decomposition were determined by using SEM, EDX, XRD and FTIR.

2. EXPERIMENTAL

Copper acetate monohydrate (Merck, purity: >99.0%) was used to as the precursor for synthesizing CuO nanoparticles. The precursor was placed approximately 0.5 g in an alumina crucible and annealed at 200, 300 and 400°C for 3 h under air atmosphere, respectively. The characterizations of products obtained from the thermal decomposition were performed by various analysis and techniques as XRD, FTIR, SEM and EDS.

2.1. Characterization

The crystal structure of products obtained from the thermal decomposition at 200, 300, and 400°C were determined by X-ray diffraction (XRD) in the 2θ range of 10-90° (PANalytical Empyrean) with a scanning speed of 2°/min at room temperature. The surface morphology and elemental analysis of the synthesized samples were analyzed by scanning electron microscope (SEM) coupled with an energy dispersive X-ray analysis (EDS) (Zeiss Sigma 300). FTIR analysis were performed in the range of 4000 to 10 cm^{-1} at the Burker VERTEX 70v Instrument. It was used to the thermogravimetric analyzer NETZSCH STA 409 PC Luxx for TG-DSC analysis. ~15-20 mg of sample was placed into a platinum crucible. The standard reference matter is the calcined α-Al_2O_3 powder. The analysis were operated at 10°C min^{-1} heating rates, and air atmosphere.

3. RESULTS AND DISCUSSION

The thermal decomposition of copper acetate monohydrate was investigated to determine its thermal behavior and decomposition temperature by TG-DTG/DSC. The experimental TG-DTG and DSC thermal decomposition graphs of $Cu(CH_3COO)_2.H_2O$ at heating rates of 10°Cmin^{-1} from 25°C to 900°C are given at Fig. 1 and 2. As can be seen Figure 1, it is seen two mass-loss regions and a tiny mass-gain region. The sample dehydrates at 110-180°C, it corresponds to endothermic peak at DSC graph (Fig.2) and the mass loss is approximately 9.17%. This weight loss is the thermal dehydration of copper acetate monohydrate, and the sample turns into anhydrous copper acetate. Then decomposition of anhydrous copper acetate causes a weight loss of 52.67% at 180-300°C, it corresponds to exothermic peak at DSC graph (Fig 2). The solid product at 180-300°C decomposes to another products and volatile components, it corresponds to exothermic peak at DSC graph and the mass loss is approximately 52.67%. Then, it is seen the mass gain from 300 to 400°C (Fig. 1). The value of the mass gain is 2.53%, but there isn't a peak at DSC curve. In the literature, it is expressed that the mass gain in the temperature range 300-400°C is related to oxidizing of Cu_2O to CuO [22].

SYNTHESIS OF COPPER OXIDE (CuO) FROM THERMAL DECOMPOSITION OF COPPER ACETATE MONOHYDRATE ($Cu(CH_3COO)_2.H_2O$)

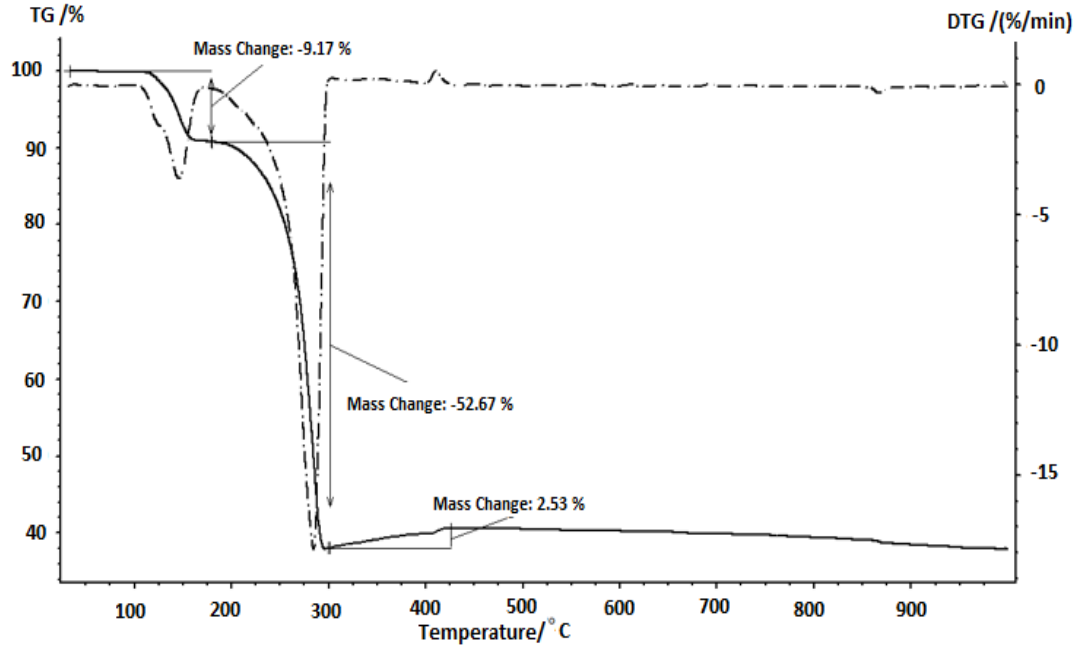


Figure 1. TG-DTG curves of $Cu(CH_3COO)_2.H_2O$

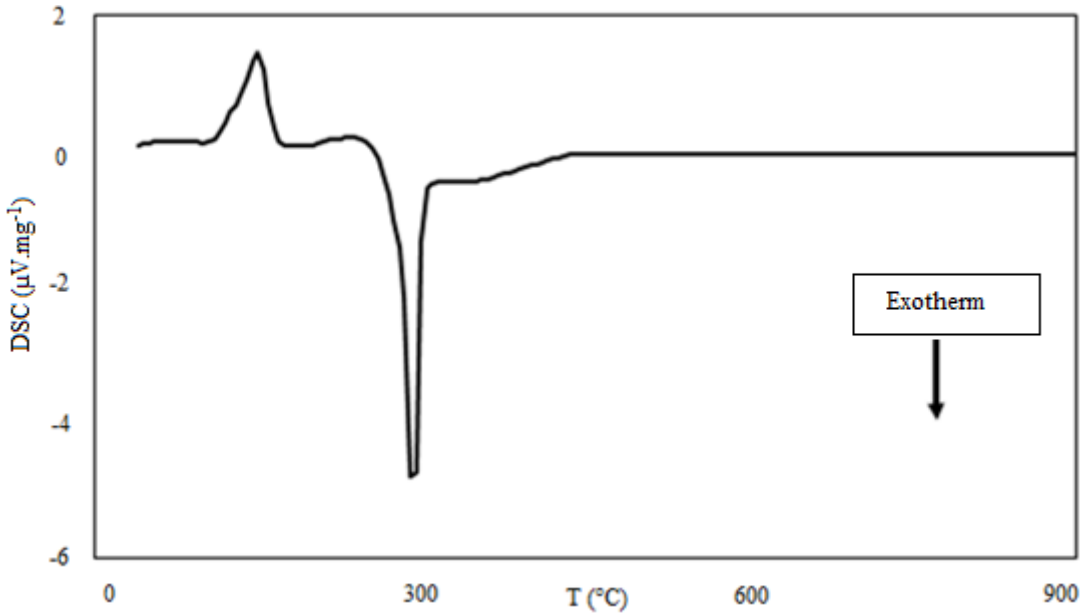


Figure 2. DSC curve of $Cu(CH_3COO)_2.H_2O$

In particularly, XRD experiments were performed to better determine the solid products at 200, 300 and 400°C at Fig. 3. It is understood that there is $Cu(CH_3COO)_2$ at 200°C, and the products at 300 and 400°C temperatures consist of Cu_2O and CuO compounds. It can be deduced from the XRD profiles that Cu_2O are progressively converted to CuO by the temperature increasing, and a small quantity of Cu_2O remains in the solid products. Fig. 3 shows that the CuO diffractions in the XRD patterns at 400°C are compatible with the standard monoclinic structure of CuO (JCDD 01-077-7718). The crystallite sizes have been calculated by Scherrer formula [24]. The calculated crystallite size decreases from 33.96 nm (300°C) to 21.06 nm (400°C) with increase temperature. ($\mu V.mg^{-1}$)

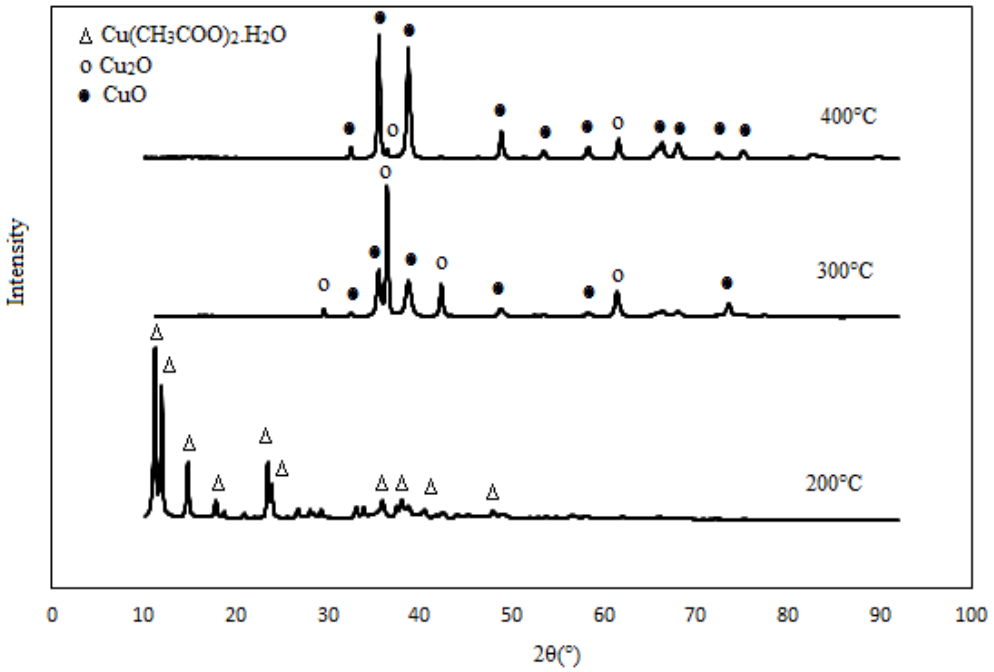


Figure 3. XRD profiles of the samples at 200, 300 and 400°C

FTIR analysis was carried out to understand the chemical structure of the products obtained at each temperatures. Fig. 4 displays the functional groups of oxidized solids at 200, 300 and 400°C temperatures. It is seen how the sample changes by the temperature increasing at Fig. 4. FTIR spectrum at 200°C displays C-O-C stretching in the range of 1250 to 1000 cm^{-1} and O-H stretching in the range of 1700 to 1500 cm^{-1}. The three characteristic bands observed at 428 cm^{-1}, 491 cm^{-1}, and 609 cm^{-1} can be assigned to CuO and Cu_2O at 300 and 400°C [3, 25]. It is usually seen the metal oxide bands (Me-O) below 1000 cm^{-1}, which is caused by interatomic vibrations. The peaks at 609 cm^{-1} and 491 cm^{-1} may be ascribed to the Cu-O stretching [26]. In this way, CuO with monoclinic structure is also verified by means of the FTIR analysis.

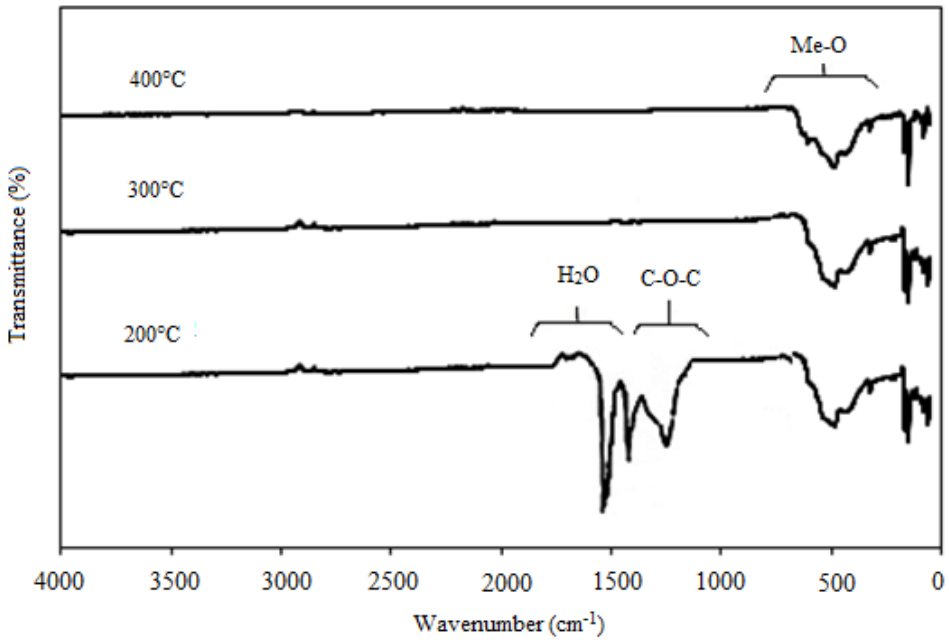


Figure 4. FTIR spectrum of the samples at 200, 300 and 400°C

SYNTHESIS OF COPPER OXIDE (CuO) FROM THERMAL DECOMPOSITION OF COPPER ACETATE MONOHYDRATE ($Cu(CH_3COO)_2.H_2O$)

SEM analysis is used to investigate the effect of the temperature on the morphology of the structure. It is given SEM micrographs of the samples obtained at 200, 300, and 400°C at Fig. 5. The sample at 200°C has a fibrous structure (Fig 5a). It is observed that the structure at 300°C is gradually deteriorating, randomly arranged and agglomeration (Fig 5b). In particularly, SEM micrograph indicates well-dispersed and regularly spherical shapes of highly crystalline CuO nanoparticles at 400°C (Fig 5c). Also, there are the cavities in the structure. The average particle size was observed to decrease by temperature increasing from SEM micrographs. This is agree with the particle size results calculated from Sherrer equation.

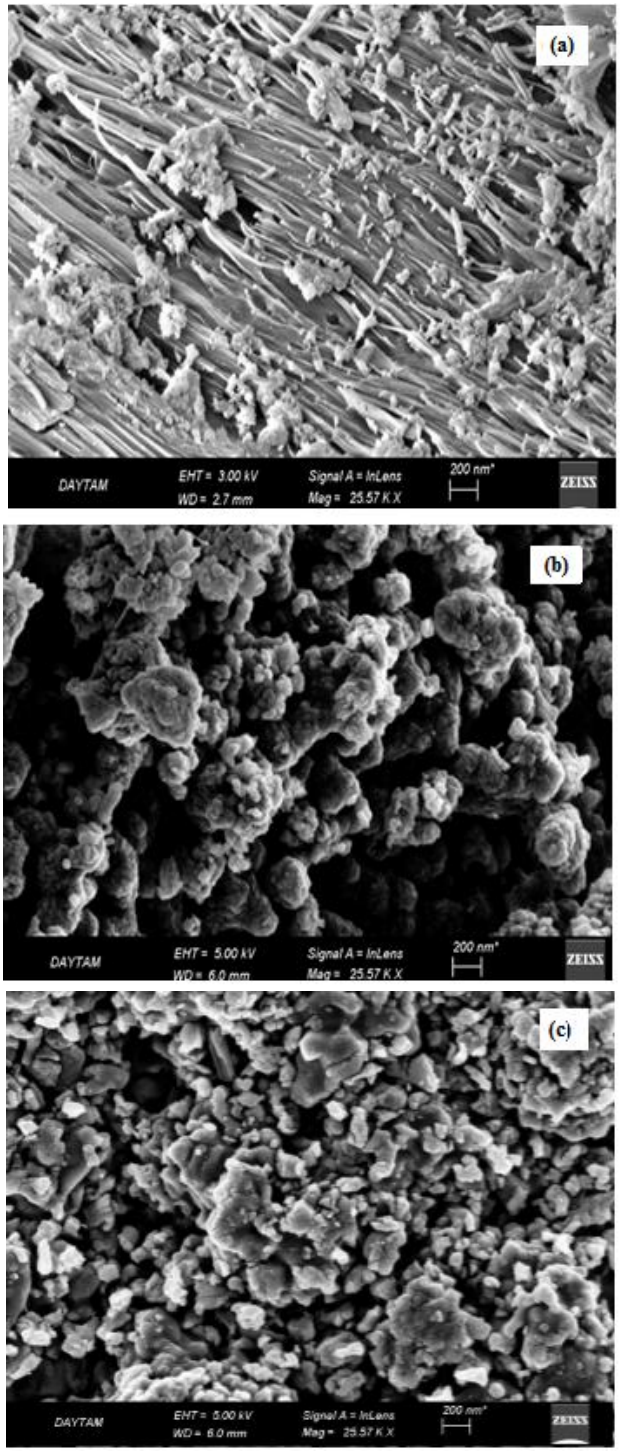
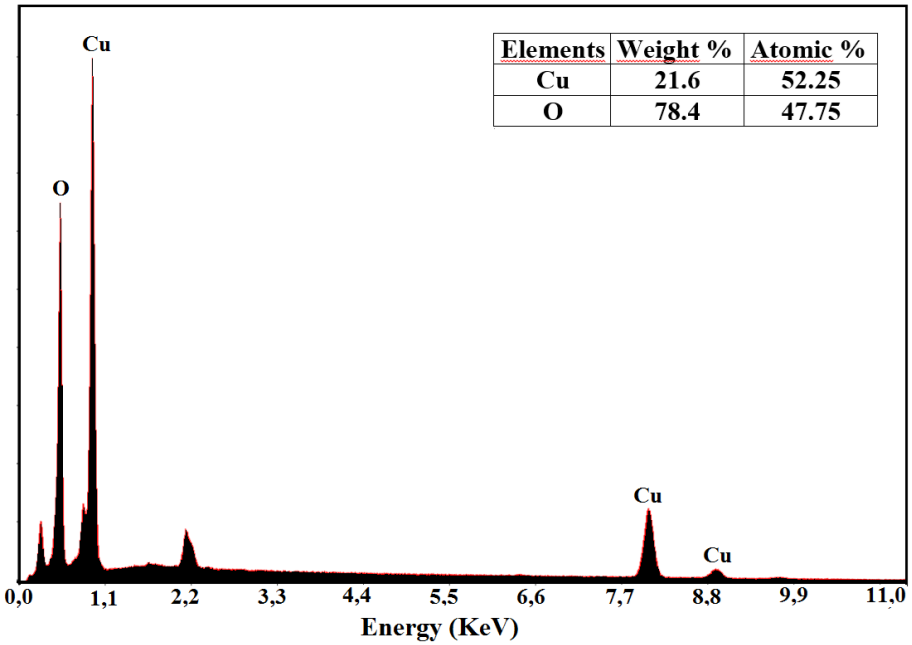


Figure 5: SEM micrographs of the samples obtained at (a) 200, (b) 300 and (c) 400°C

The elemental quantification and stoichiometry ratio of the annealed samples at 400°C were confirmed by EDS analysis. The EDS spectrum detected the Cu and O atoms without any other unknown impurity (Fig. 6). The peak observed at about 2 keV is the gold signature obtained from the surface coating of the samples. The spherical CuO nanoparticles are evaluated by EDX quantitative analysis software. It shows the uniform distribution of copper (52.25 % of Cu and 47.75 % of O). If it displays in atomic %, theoretically Cu will be 50% and O will be 50%. It is experimentally found 52.25 % of Cu and 47.75 % of O, because of a small quantity of Cu_2O remains in the solid products.



Elements	Weight %	Atomic %
Cu	21.6	52.25
O	78.4	47.75

Figure 6. EDS analysis for sample obtained at 400°C from thermal decomposition of $(Cu(CH_3COO)_2.H_2O)$

4. CONCLUSION

Utilizing a simple and quick method, the synthesis of CuO nanoparticles in high purity by way of thermal decomposition of copper acetate monohydrate $(Cu(CH_3COO)_2.H_2O)$ in an air atmosphere was carried out. TG-DTG/DSC analyzes were performed to understand better the process of $(Cu(CH_3COO)_2.H_2O)$. It was seen from TG-DTG/DSC analyzes that the thermal decomposition process consists of three main steps (two mass-loss regions and a tiny mass-gain region). The structural properties of CuO nanoparticles obtained at 200, 300 and 400°C were investigated out using XRD, FTIR, SEM and EDS analysis. The FTIR analysis displayed a broad absorption band related to Cu-O vibration band. The XRD analysis supported that the synthesized CuO nanoparticles with a small quantity Cu_2O have monoclinic structure. In addition, the SEM results showed the formation of spherical shaped nanoparticles.

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