


# GRAFEN OKSİT ÜRETİMİNDE pH DEĞERİ ETKİSİNİN ARAŞTIRILMASI

## INVESTIGATION THE EFFECT OF pH VALUE IN GRAPHENE OXIDE PRODUCTION

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### ÖZET

Son yıllarda grafen oksit (GO) ileri teknoloji uygulama alanlarında kullanımı büyük ilgi çekmektedir. GO, çeşitli fonksiyonel grupları içeren bir karbon bazal düzleminden oluşmaktadır. GO, özellikleri sayesinde eklendiği malzemelerin özelliklerini iyileştirebilir. Bu nedenle GO çeşitli fotokatalitik, sensör ve pil uygulamalarında kullanılmaktadır. Ayrıca, yüksek elektriksel iletkenlik, termal iletkenlik ve yüksek yüzey alanı gibi olağanüstü özelliklere sahip olan grafenin büyük ölçekli üretimi GO'nun indirgenmesi ile mümkündür. Bu nedenle kaliteli ve kontrol edilebilir GO üretimi gereklidir. GO genellikle endüstriyel olarak üretime uygun bir kimyasal yöntem olan Hummer's Metodu ile üretilmektedir. Hummer's Yönteminde grafitin oksitleyici ajanlar yardımıyla oksitlenmesi ile grafit oksit elde edilmektedir. Grafit oksidin ekfoliyasyonu ile de GO elde edilmektedir. Ancak orijinal Hummer's Metodu, tehlikeli ve zararlı gazların emisyonu ve düşük verimi nedeniyle birçok dezavantaja sahiptir. Geçmişten günümüze araştırmacılar tarafından birçok Hummer's Metodu geliştirilmiştir. Çeşitli modifikasyonlar sonucunda verimli, toksik olmayan ve zararsız üretim yöntemi aşamaları içeren Modifiye Hummer's Metodu, GO üretiminde kullanılmak üzere tercih edilmektedir. Üretimin her aşaması, elde edilen GO'nun yapısını ve özelliklerini etkilemektedir. GO üretim parametrelerinin etkisini anlamak, elektronik, optik, biyolojik ve grafen üretim uygulamalarında kullanımı için önemlidir. Hummer's Metodunda grafitin oksidasyonundan sonra safsızlıkları gidermek için hidroklorik asit (HCl) ve sonrasında saf su ile yıkama işlemi uygulanmaktadır. Son aşama olan yıkama süreci GO'nun nihai yapı özellikleri için önemli bir aşamadır. Bu çalışmada, geliştirdiğimiz Modifiye Hummer's Metodu kullanılarak pH etkisinin elde edilen GO yapısına etkisi incelenmiştir. Farklı pH seviyelerindeki çözeltilerden elde edilen GO numunelerinin X-Işını Difraktometresi (XRD), Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR) ve Ultraviyole - Görünür Spektrofotometresi (UV-Vis) kullanılarak yapısal karakterizasyon çalışmaları yapılmıştır.

Elde edilen sonuçlara göre çözeltili pH seviyesindeki farklılığın GO'nun yapısını değiştirdiği ve eksfolasyon derecesinde farklılık gösterdiği belirlenmiştir.

**Anahtar Kelimeler:** Grafen oksit, pH, Saflaştırma, Geliştirilmiş Hummer's, XRD, FTIR

## ABSTRACT

In recent years, the use of graphene oxide (GO) in advanced application areas has attracted great interest. GO consists of a carbon basal plane containing various functional groups. Thanks to its properties, GO can improve the properties of the materials to which it is added. Therefore, GO is used in various photocatalytic, sensor and battery applications. Moreover, large-scale production of graphene, which has outstanding properties such as high electrical conductivity, thermal conductivity, and high surface area, is possible by reduction of GO. Therefore, quality and controllable GO production is required. GO is generally produced with the Hummer's Method, which is a suitable chemical method for industrial production. In Hummer's Method, graphite oxide is obtained by oxidizing of graphite with the help of oxidizing agents. Afterwards, GO is obtained by exfoliating of the graphite oxide. However, the original Hummer Method has many disadvantages due to the emission of harmful, dangerous gases and its low efficiency. Many Hummer's methods have been derived by researchers from past to present. As a result of various modifications, the Modified Hummer's Method, which includes efficient, non-toxic and harmless production method steps, was preferred in GO production. Each stage of production process affects the properties and structures of the obtained GO. Understanding the effect of GO production parameters on GO structure, is important for its use in electronics, optics, biological, and graphene production applications. In Hummer's Method, after the oxidation of graphite, washing with HCl followed by distilled water is applied to remove impurities. The final step, which is the washing process, is an important step for the final structure properties of GO. In this study, the effect of pH value on the obtained GO structure was investigated by using the Modified Hummer's Method that we developed. Structural characterization studies of GO samples from solutions at different pH levels were performed using X-Ray Diffractometry (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Ultraviolet - Visible Spectrophotometer (UV-Vis). According to the obtained results, it was determined that the difference in pH level of solution changed the structure of GO and affected the degree of exfoliation.

**Keywords:** Graphene oxide, pH, Purification, Modified Hummer's, XRD, FTIR.

## INTRODUCTION

Graphene and graphene based materials are widely used in various applications such as sensors [1], batteries [2], medical applications [3], composites and photocatalytic materials [4,5]. Graphene oxide (GO) is one of the most important precursors for graphene materials. GO has been widely used both in research and industrial production due to its excellent chemical processability and production scalability [6]. GO has a similar hexagonal carbon structure to graphene but also contains hydroxyl (-OH), alkoxy (C-O-C), carbonyl (C=O), carboxylic acid (-COOH) and other oxygen-based functional groups [7]. The carbons in the C-C/C=C bonds are sp<sup>2</sup> hybridized structures and additionally, in the oxidized regions, carbon bonds have sp<sup>3</sup> hybridization due to functional groups. As stated by many researchers, GO can be dispersed in aqueous environments and improves the properties of the materials due to the functional groups on its basal plane surface. In addition, aqueous solutions of GO are acidic due to the carboxylic acid and sulfate functional groups on its structure [8-10]. Furthermore, the functional groups of GO can be altered by changing the production stages and its electrical, optical and chemical properties can be modified into a suitable structure according to application areas [11].

The first work on the synthesis of GO material was done by Benjamin Brodie in 1859 [12]. Small amount of potassium chlorate was added to solution of graphite and nitric acid (HNO<sub>3</sub>) in this method.

It was modified in 1898 [13] by forming a mixture of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and  $\text{HNO}_3$  to produce highly oxidized GO, followed by the gradual addition of potassium chlorate to the reaction mixture. An developed method for GO production, known as the Hummers method, was introduced by Hummers and Offeman in 1958 [14]. In this method, GO was obtained by oxidation of graphite powder to graphite oxide by using concentrated  $\text{H}_2\text{SO}_4$  as intercalator, potassium permanganate ( $\text{KMnO}_4$ ) and sodium nitrate ( $\text{NaNO}_3$ ) as strong oxidizing agents. GO is obtained after washing with distilled water. Although the Hummers method is the most widely used method for GO production by researchers due to its high efficiency, ease and reaction safety advantages, it has some disadvantageous due to the release of toxic gases during the oxidation process and the difficulty removing residual  $\text{Na}^+$  and  $\text{NO}^-$  ions during the GO purification step [15]. Therefore, Marcano et al. [16] developed the modified Hummers method in 2010 by increasing the amount of  $\text{KMnO}_4$  instead of  $\text{NaNO}_3$  and performing the reaction in a 9:1 sulfuric acid/phosphoric acid ( $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ ) mixture. This modification is successful for increasing reaction efficiency and reducing toxic gas formation.

The product obtained after the oxidation process is graphite oxide. Graphite oxide must be exfoliated to obtain GO structure. There are various exfoliation processes that can be applied to convert graphite oxide into several or single-layer graphene oxide structures. These are generally sonication, mixing and centrifugation processes [16–18]. However, there are different studies that carry out the washing stages and the exfoliation stage at the same time or separately. In a study of Panwar et al. [5], the GO slurry was washed with 1:10 HCl solution and followed by washing with distilled water until the pH was between 5 and 7. They were stated that GO was produced by increasing exfoliation with centrifugation and sonication processes. In a different study by Hou et al. [19], graphite oxide was washed with distilled water until the pH was 7 in the purification stages after oxidation process. Then, GO was obtained by application of sonication process, after the washing step of graphite oxide. In another study by Marcano et al., GO was obtained after washing with HCl, distilled water and ethanol using filtration and centrifugation after oxidation of graphite. Yadav et al. [20], performed different purification procedures in the GO production. Firstly, GO was washed with 10% HCl solution. Then, it was stated that GO was washed with distilled water by centrifugation until pH neutral and GO was obtained.

In this study, it was aimed to determine the effect of pH level on the GO structure. GO was produced with the Modified Hummer's Method. For this purpose, after oxidation step, GO was firstly washed with a HCl solution during the purification stages. Then, washing processes were carried out with distilled water until the pH of GO was between 4 and 5. Mixing and centrifugation were performed at each washing step and then the pH of GO was measured. For this purpose, GO samples were dried by taking samples at a pH value of GO approximately 1-2, 2-3, 3-4 and 4-5 ranges. Afterward, structural characterization studies of GO samples were carried out by using XRD, FTIR and UV-Vis spectrophotometers.

## **2. EXPERIMENTAL**

### **2.1. Materials**

Graphite powder (<20  $\mu\text{m}$ ) was purchased from Sigma Aldrich.  $\text{H}_3\text{PO}_4$  (85%),  $\text{H}_2\text{SO}_4$  (95-97%),  $\text{H}_2\text{O}_2$  (35%) and  $\text{KMnO}_4$  (99%) were purchased from Isolab Chemicals. All chemicals were used as received without further purification.

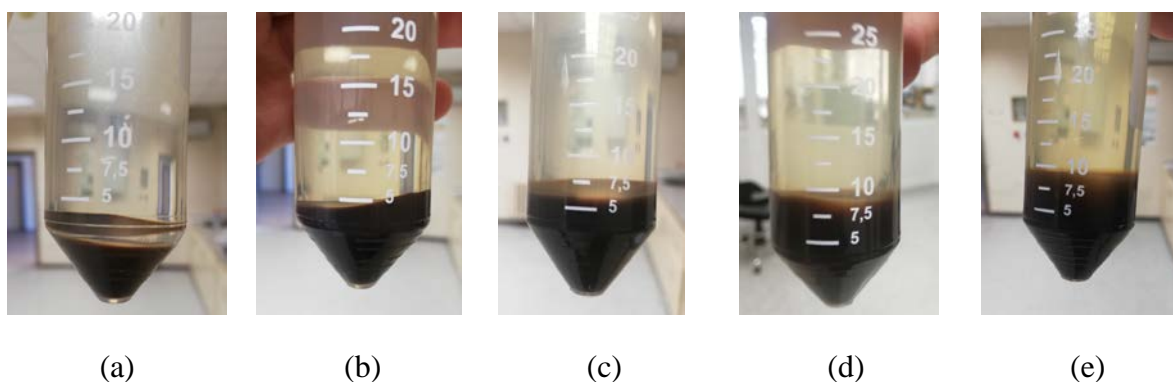
### **2.2. Production and Characterization of GO**

Modified Hummer's Method was used to produce GO. Graphite powder,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  mixture stirred for pre-exfoliation process. Afterwards,  $\text{KMnO}_4$  was added to the mixture and stirred for 2 hours. Then, distilled water was added slowly to avoid a rapid temperature increase and the temperature was gradually increased to  $95\pm 5^\circ\text{C}$  and stirred for 1 hour. Finally,  $\text{H}_2\text{O}_2$  and ice mixture were added to stop the oxidation reactions. The reaction product was washed with HCl solution to remove impurities and centrifuged (NF1200R, Nuve) to dissociate the supernatant. In this step, the

metallic ions and impurities in the GO solutions are converted to the chloride structure. Finally, GO solution was washed with distilled water to remove the chloride salts and other impurities. The degree of purification of GO is determined by measuring the pH of the GO solution after centrifugation. Washing step was carried out until the pH level reached to about 5. The pH value of the GO solution was measured with a pH meter (pH3110 to WTW Profile) after each washing step. Four GO samples were taken at different pH values between 1-2, 2-3, 3-4 and 4-5 ranges (Table 1) to investigate effect of pH value. The images of GO samples at preparation step are shown in Figure 1. Finally, obtained GO samples were dried overnight at 45°C.

**Table 1.** pH values of GO supernatant.

Samples	pH Value
P1	1.65
P2	2.62
P3	3.4
P4	4.53



**Figure 1.** Images of GO samples; a) GO obtained after 3 times washing process, Samples b) P1, c) P2, d) P3 and e) P4.

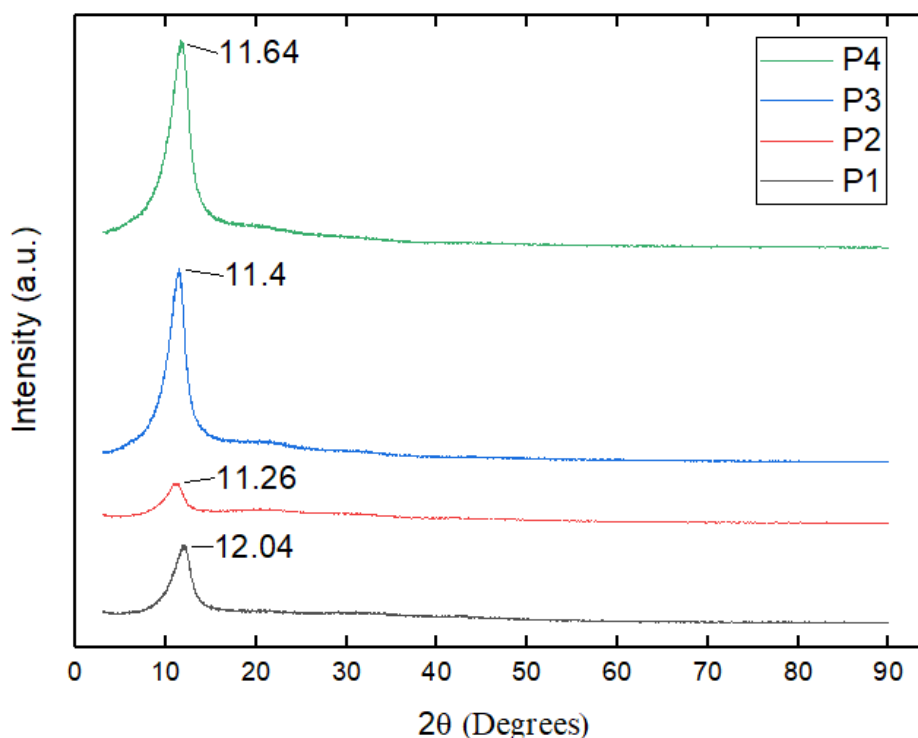
XRD analysis (Rigaku DMax-2100 PC) was performed using Cu K $\alpha$  radiation ( $\lambda=0.154$  nm) with a scan rate of 1°C/min to determine the obtained GO structure and interplanar spacing between GO layers. FTIR spectra was recorded with Thermo Scientific FTIR Spectroscopy with attenuated total reflectance (ATR) module to determine functional groups on GO basal planes. FTIR analysis was performed with a scanning range of 4000-525 cm $^{-1}$  and a resolution of 1 cm $^{-1}$ . UV-Vis analysis were performed by using Thermo Scientific Evolution 260 BIO UV Spectrophotometer in order to determine the sp $^2$  conjugation in the GO structure.

### 3. RESULTS AND DISCUSSION

In Figure 1, it is observed that GO swells by absorbing water after washing step. GO structure increased its volume after washing step as seen in Figure 1 (b), (c) and (d) compared to the structures obtained after 3 times washing with HCl as seen in Figure 1 (a). The reason of GO structure swelling is water causes a strong electrostatic repulsion force between the layers [8,13]. Also, water enters between the GO layers and exfoliates layers with the effect of centrifugation and mixing [17,18].

XRD analysis of the GO samples taken from different pH levels are shown in Figure 2. It was determined that pure GO structure was obtained and there was no different phase other than GO. The characteristic peak of the (001) plane of the GO was located around 11° [21]. In the obtained XRD results, it was determined that the main characteristic peak of the P1 sample was at 12.05° and the

main characteristic peaks of the P2, P3 and P4 samples were at  $11.26^\circ$ ,  $11.44^\circ$  and  $11.64^\circ$ , respectively. The distance between the graphene oxide layers (interplanar spacing) was calculated according to Bragg's Law [22] and given in Table 2. Distance between the layers varied with washing process. Since there was an exfoliation and the distance between the layers increased from P1 structure to P2 structure with the centrifugation process [17,18]. However, while the washing processes was progressed, interlayer distance of GO was reduced according to XRD results. The covalently bound sulfates are removed from the GO basal structure by hydrolysis during the washing processes, thus reducing the interlayer distance of GO [8]. It was known that these sulfates and carboxylic acids in the structure are responsible for the acidity of GO. Since the pH increases with the increasing washing steps, it was inferred that the functional groups attached to graphene basal plane are removed and so, the distance between the GO layers decreases. The reason why there is no change in the volume of GO after certain washing in Figure 1 is due to this situation.



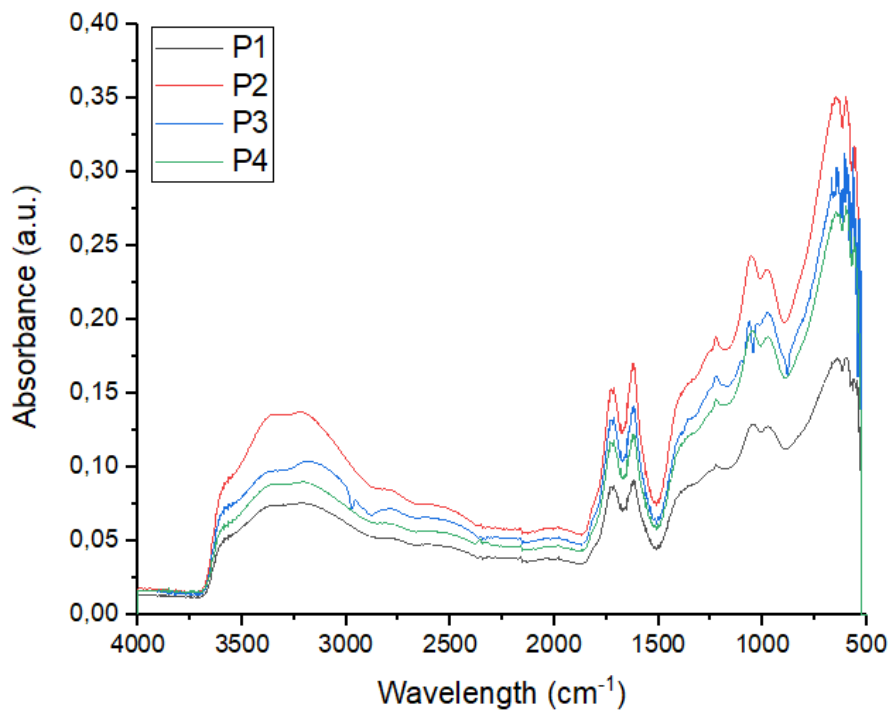
**Figure 2.** XRD analysis of the GO samples received from different pH values.

**Table 2.** Interplanar spacing (d) and 2-theta values of GO structures.

Sample	$2\theta$ ( $^\circ$ )	d ( $\text{Å}^\circ$ )
P1	12.04	7.34
P2	11.26	7.85
P3	11.44	7.72
P4	11.64	7.59

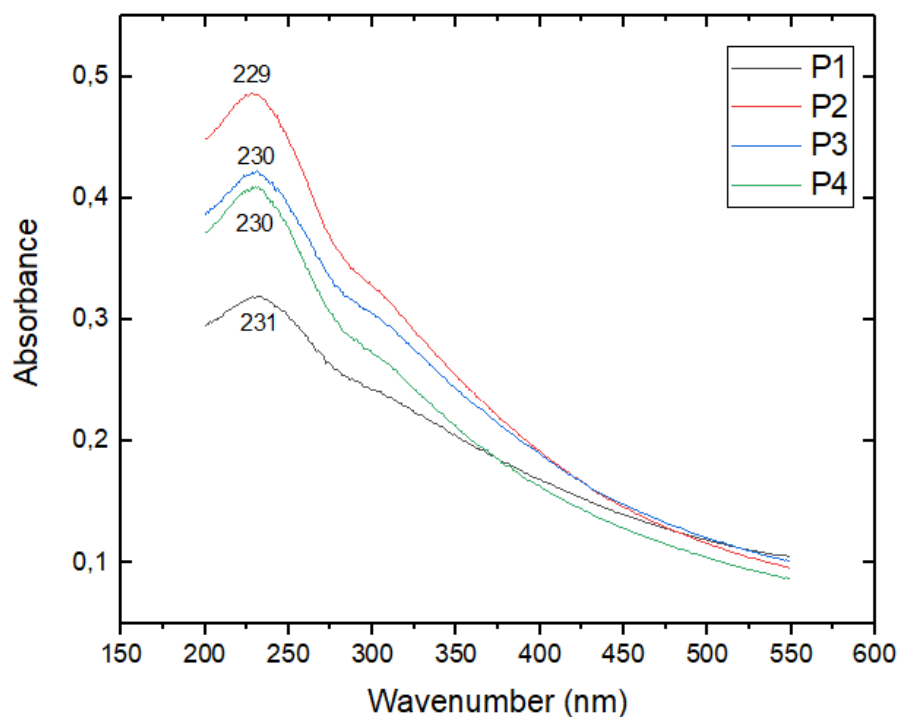
The results of the FTIR analysis are shown in Figure 3. According to the results of the FTIR analysis, the stretching vibration of the hydroxyl groups (O-H) between  $3600\text{-}2400\text{ cm}^{-1}$ , the carbonyl (C=O) group at  $1730\text{ cm}^{-1}$ , the stretching mode of the C=C  $\text{sp}^2$  carbon skeletal mesh at  $1617\text{ cm}^{-1}$ , symmetric and asymmetric stretching of the S = O bond at  $1417\text{ cm}^{-1}$  and epoxy groups (C-O-C) at  $1050\text{ cm}^{-1}$  were observed in all GO samples [18,20]. According to the obtained result, it was determined that all

functional groups that should be present in the GO structure. When the intensity of functional groups was compared, it was determined that the intensity of the functional groups in the P1 sample was lower, but the functional groups in the P2 sample increased with exfoliation process. With further washing process, the intensity of functional groups are reduced as the functional groups are removed from the basal plane [23]. This result supports the decrease of distance between the layers with further washing process obtained from XRD analysis.



**Figure 3.** FTIR analysis of the GO samples received from different pH values.

The results of UV-Vis analysis are depicted in Figure 4. The UV-Vis spectrum of GO has two characteristic absorbance bands that are used to determine oxidation of graphene oxide and the amount of  $sp^2$  conjugate structure. The absorbance band around 230 nm indicates the  $\pi \rightarrow \pi^*$  electron transition of carbon aromatic bonds ( $sp^2$ ). The second characteristic peak is around 300 nm. This peak indicates the  $n \rightarrow \pi^*$  electron transition of the C=O bond. According to results, the maximum point of the carbon aromatic bond electron transition of the P2 sample was 229 nm and it was determined that it shifted to the left compared to the P1 sample (231 nm). This is due to the exfoliation of GO in the P2 step with the centrifugation and mixing effect [17,18]. FTIR and XRD results also support UV-Vis results. However, it was observed that the electron transition band of the carbon aromatic bond shifted to the right with increasing washing steps. At this stage, it is due to the reorganization of the  $sp^2$  hybridization in the GO basal plane where the covalently bound sulfates in the basal plane interact with water and separate from the structure with washing [8,23]. Therefore, it shifts to the right due to the increase in  $sp^2$  conjugate structure.



**Figure 4.** UV-Vis analysis of the GO samples received from different pH values.

#### 4. CONCLUSIONS

According to the obtained results, it was determined that exfoliation and oxidation degree of GO increased by centrifugation during the washing process. According to the XRD results, it was found that the structure of samples consisted of GO and there was no different phase in the structure for all samples. It was assigned that the distance between the GO layers decreased due to the loss of functional groups with further washing steps. It was determined that the  $sp^2$  hybridization in the structure increased after a certain pH value. It has been found that the final GO can contain different degrees of functional groups depending on the pH level.

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