

## A Fast Method for Synthesis Magnesium Hydroxide Nanoparticles, Thermal Stable and Flame Retardant Poly vinyl alcohol Nanocomposite

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*Article history:*

Received 13/6/2014

Accepted 28/8/2014

Published online 1/9/2014

*Keywords:*

Nanoparticles

Nanocomposite

Thermal Stability

PVA

### Abstract

Magnesium hydroxide nanostructures as an effective flame retardant were synthesized by a facile and rapid microwave reaction. The effect of different surfactants such as cationic, anionic and polymeric on the morphology of magnesium hydroxide nanostructures was investigated. Nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. The influence of  $Mg(OH)_2$  nanostructures on the thermal stability and flame retardancy of the poly vinyl alcohol (PVA) matrix was studied using thermogravimetric analysis (TGA) and UL-94 respectively. Thermal decomposition of the nanocomposites shift towards higher temperature in the presence of  $Mg(OH)_2$  nanostructures. The enhancement of thermal stability and flame retardancy of nanocomposites is due to the endothermic decomposition of  $Mg(OH)_2$  and release of water which dilutes combustible gases.

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### 1. Introduction

The most commonly used mineral flame retardants are aluminum hydroxide and magnesium hydroxide. As the temperature rises magnesium hydroxide shows an endothermic decomposes (1.356 kJ/g) about 330°C and absorbs energy. Moreover, it releases nonflammable water which dilutes combustible gases. Residual magnesium oxide also provides heat insulation by reflecting heat when it accumulates on the surface. Magnesium hydroxide is used as halogen-free flame-retardant for polymers.  $Mg(OH)_2$  can act simultaneously as a

reinforcing agent, flame retardant and smoke suppressant additive with low or zero emissions of toxic or hazardous substances [1–6]. The main advantages of polymer materials over many metal compounds are high toughness, corrosion resistance, low density and thermal insulation. Improvement of the flame retardancy and thermal stability of polymers is a major challenge for extending their use for most applications. The use of halogen-free flame retardants is widespread due to the increasing concern about the health and environmental risks [7-9]. One of the main

disadvantages of magnesium hydroxide is that for effective flame retardancy tests high loading levels are required to achieve the appropriate fire retardancy. Increasing the loading of inorganic metal hydroxides will result in a significant decrease in physical properties. The higher level of flame retardancy of nanoparticles is due to their bigger surface to volume fractions which let them disperse into the polymeric matrix homogeneously, and hence leads to formation of a compact char during the combustion [10-17]. Poly vinyl alcohol has been widely used in a wide range of applications due to its particular advantages. It is a water soluble biodegradable polymer with applications in paper coating, packaging films and adhesives. The scientific literature contains very diverse strategies for improving fire resistance of PVA [1,2]. The physical and chemical properties of nanoparticles are greatly influenced by their shape and size distribution as well as their agglomerated state and dispersion property, which are strongly related to the preparation process. In this work a facile and rapid method for preparation of magnesium hydroxide is used. Magnesium hydroxide was then added to the poly vinyl alcohol in order to increase the thermal stability and flame retardant properties.

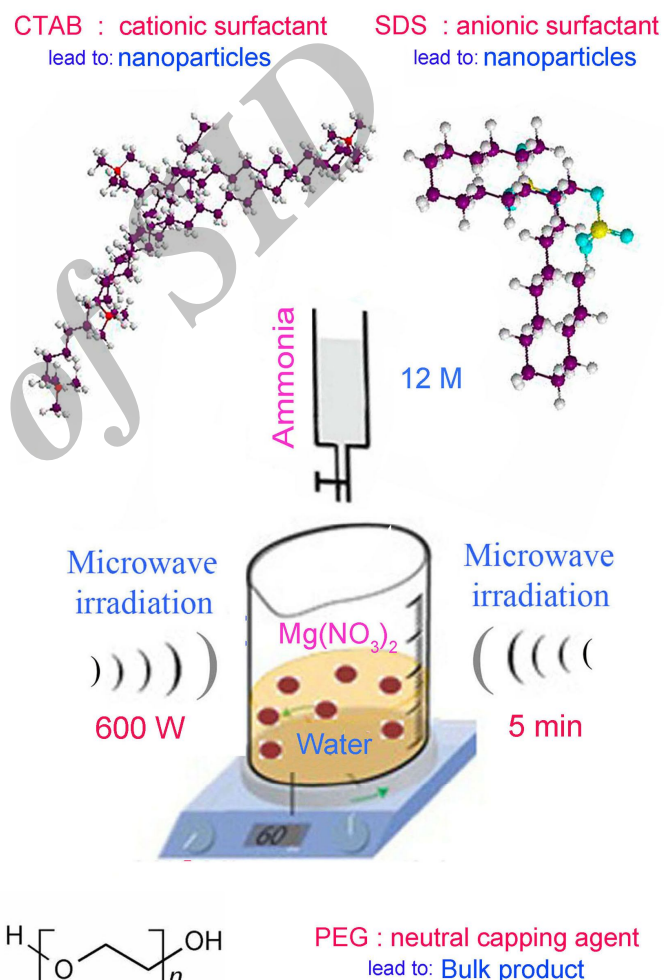
## 2 Experimental

### 2.1 Materials and characterization

$Mg(NO_3)_2 \cdot 6H_2O$ , ammonia, sodium dodecyl sulfonate (SDS), cetyl tri-methyl ammonium bromide (CTAB), poly vinyl alcohol (PVA MW:20000-30000) and poly ethylene glycol (MW: 10000, 20000) were purchased from Merck.

All the chemicals were used as received without further purifications. X-ray diffraction (XRD) patterns were recorded by a Philips X-ray diffractometer using Ni-filtered  $CuK_\alpha$  radiation. A multi-wave ultrasonic generator (Bandeline MS 73) equipped with a converter/transducer and titanium oscillator operating at 20 kHz with a maximum power output of 100 W was used for the ultrasonic irradiation. Scanning electron microscopy (SEM)

images were obtained using a LEO instrument (Model 1455VP). Prior to taking images, the samples were coated by a very thin layer of Pt (BAL-TEC SCD 005 sputter coater) to make the sample surface conducting obtain better contrast and prevent charge accumulation. In UL-94 a bar shape specimen of plastic  $130 \times 13 \times 1.6$  mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each).



**Fig. 1.** Schematic diagram of  $Mg(OH)_2$  nanostructures preparation

### 2.2. Synthesis of $Mg(OH)_2$ nanoparticles

1g  $Mg(NO_3)_2 \cdot 6H_2O$  and 0.25 g of surfactant were dissolved in water. 20 mL of ammonia (12 M), was slowly added into the solution under microwave

irradiation at 600 W (5 minutes, 30s on : 30s off). The white precipitate was centrifuged and washed with distilled water to removing the surfactant, and later dried at 70°C for 24h in a vacuum dryer. These stages carried out for four surfactant materials as synergetic additives including PEG, CTAB and SDS. Schematic of preparation of  $Mg(OH)_2$  nanostructures and effect of various surfactants on morphology of the products is depicted in Fig. 1.

### 2.3. Synthesis of PVA- $Mg(OH)_2$ nanocomposite

4 g of PVA was dissolved in 10 mL of water and then  $Mg(OH)_2$  (1 g) was dispersed in 5 mL of water with ultrasonic waves (60W, 30 min). The dispersion of  $Mg(OH)_2$  was then added slowly to the polymer solution. The solution was mixed under stirring for 6 h. For preparation of samples for UL-94 test after stirring, the product was casted on a template with dimension  $130 \times 13$  mm and after about 48 h of solvent evaporation; the nanocomposite was placed in the vacuum oven for another 6 h for removal of residual traces of water. The final sheets for the test are  $130 \times 13 \times 1.6$  mm in dimension (stay at oven 90 °C for 48 h) (Fig. 2).

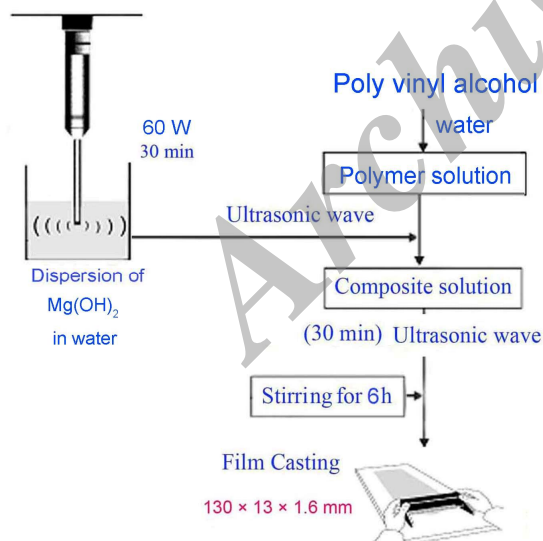


Fig. 2. Preparation of PVA- $Mg(OH)_2$  nanocomposite

## 3. Results and discussion

XRD pattern of  $Mg(OH)_2$  nanoparticles is shown in Fig. 3. It is indexed as a pure hexagonal structure

with suitable agreement to literature value (reference peaks are also depicted in the XRD pattern, JCPDS card no. 78-0316, Space group: P-3m1).

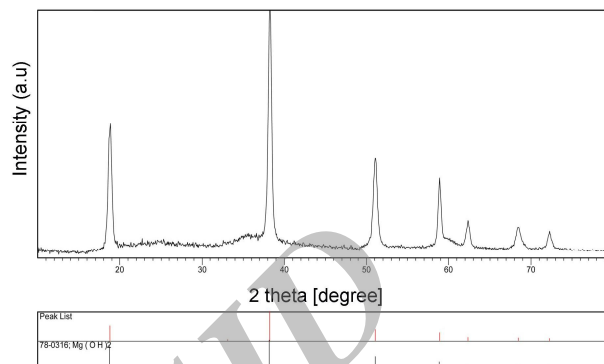


Fig. 3. XRD pattern of  $Mg(OH)_2$  nanoparticles

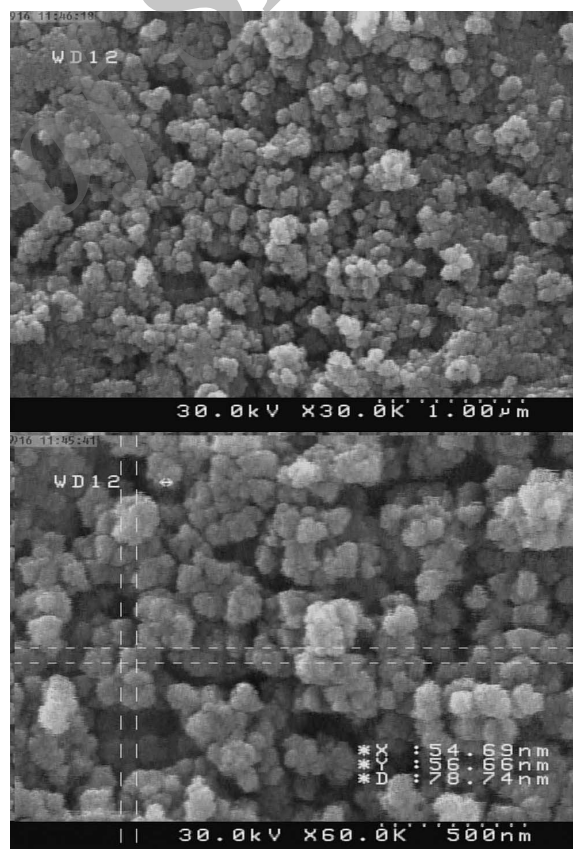


Fig. 4. SEM images of  $Mg(OH)_2$  nanoparticles obtained by CTAB

SEM images of  $Mg(OH)_2$  synthesized by different surfactants cationic, anionic and neutral are shown in Fig. 4-6 respectively. By using cetyl tri-methyl ammonium bromide (CTAB: as a cationic

surfactant) nanoparticles with average diameter of 50 nm were obtained (Fig. 4). Surfactant as a capping agent lead to nucleation step become predominant compare to growth stage. By applying sodium dodecyl sulfonate (SDS as an anionic surfactant, Fig. 5) nanoparticles with mediocre size of 60 nm were synthesized. Fig 6a and 6b illustrate products which are synthesized by various molecular weight of poly ethylene glycol 10000 and 20000 respectively. PEG as a neutral capping agent lead to agglomerated and bulk products. It seems PEG remained on the surface of particles and growth stage overcomes to nucleation stage and bulk products were obtained.

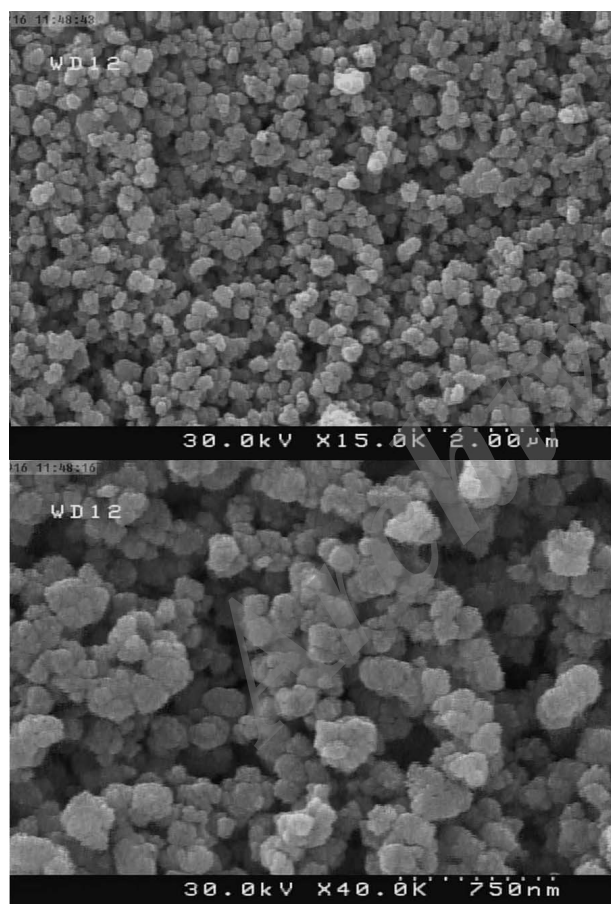


Fig. 5. SEM images of nanoparticles synthesized by SDS

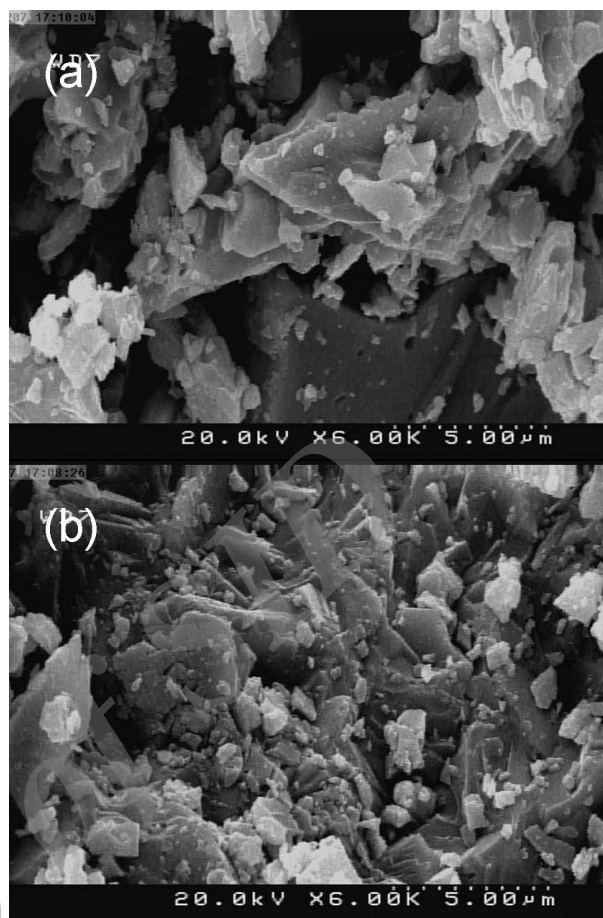


Fig. 6. SEM images obtained by (a) PEG 10000 (b) PEG 20000

FT-IR spectrum of the  $\text{Mg}(\text{OH})_2$  is shown in Fig. 7; absorption at  $3390\text{ cm}^{-1}$  is related to O-H bond of adsorbed water. Sharp peak at  $3668\text{ cm}^{-1}$  is attributed to the O-H bond stretching vibration in the crystal structure. Absorption at around  $423\text{ cm}^{-1}$  is assigned to the Mg-O stretching vibration in  $\text{Mg}(\text{OH})_2$  [1, 3].

TGA curves of pure PVA and PVA- $\text{Mg}(\text{OH})_2$  nanocomposite are illustrated in Fig. 8a and 8b respectively. According to curves thermal decomposition of PVA- $\text{Mg}(\text{OH})_2$  shifts towards higher temperature in the presence of  $\text{Mg}(\text{OH})_2$  and initial degradation temperature ( $T_{\text{onset}}$ ) was increased in compare with pure polymer.

The enhancement of thermal stability of nanocomposites is due to endothermic decomposition of  $\text{Mg}(\text{OH})_2$  that absorbs energy and simultaneously release of water which dilutes

combustible gases. Exfoliated  $\text{Mg}(\text{OH})_2$  have also a barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer. Adsorption of polymer chains onto the surface of  $\text{Mg}(\text{OH})_2$  nanoparticles results in a restriction of the segmental mobility and suppress chain-transfer reactions [1-3]. DTA curves of pure polymer and nanocomposites are shown in Fig. 9a and 9b. Due to the presence of magnesium hydroxide (endothermic decomposition and absorbs energy) DTA curve of the nanocomposite obviously shows endothermic peaks.

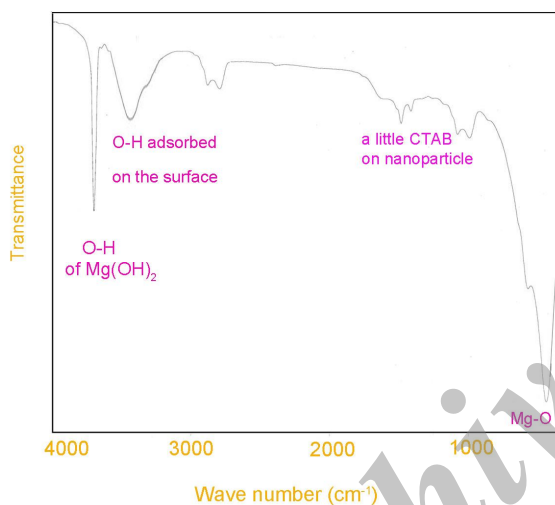


Fig. 7 FT-IR of  $\text{Mg}(\text{OH})_2$  nanoparticles

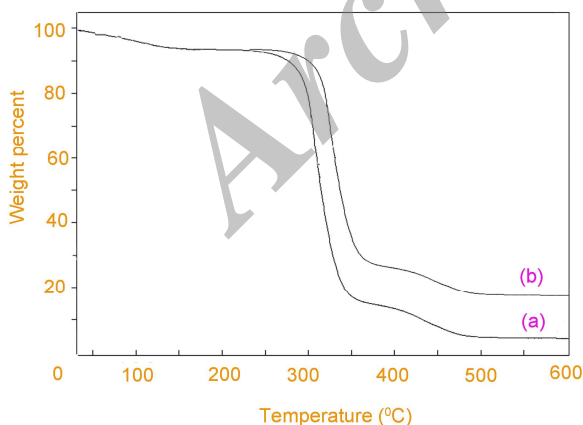


Fig. 8. TGA graphs of (a) pure PVA (b) PVA- $\text{Mg}(\text{OH})_2$  nanocomposite

In PVA- $\text{Mg}(\text{OH})_2$ , nanoparticles have been appropriately distributed in PVA matrix and

because of hydrogen bonds between them a suitable barrier layer of nanoparticles is formed.

The effect of nanostructure on flame retardant properties has been considered using UL-94 test. In UL-94 a bar shape specimen of plastic  $130 \times 13 \times 1.6$  mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each). A V-0 classification is given to material that is extinguished in less than 10 s after any flame application, drips of particles allowed as long as they are not inflamed. A V-1 classification is received by a sample with maximum combustion time  $< 30$  s, drips of particles allowed as long as they are not inflamed. The sample is classified V-2 if it satisfies the combustion time criteria of V-1, but flaming drips are allowed. Materials are ranked as N.C. in UL-94 tests when the maximum total flaming time is above 50 s. The sample is classified HB when slow burning on a horizontal specimen; burning rate  $< 76$  mm/min [5,16,17].

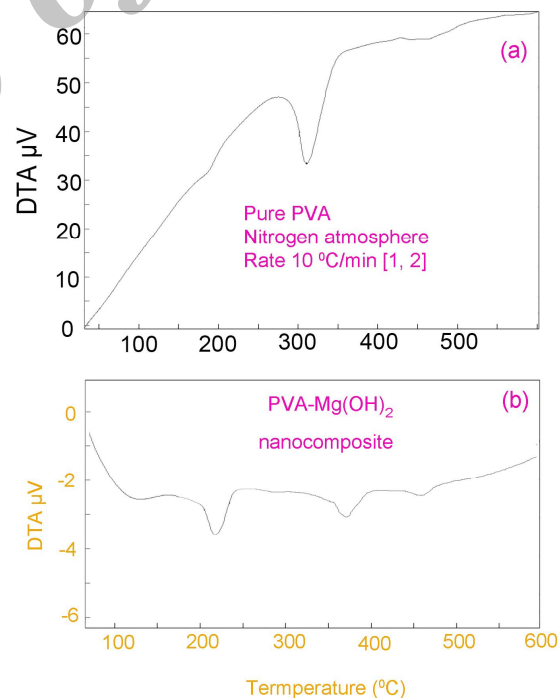


Fig. 9. DTA curves of (a) pure PVA (b) PVA- $\text{Mg}(\text{OH})_2$  nanocomposite

UL-94 tests for PVA and PVA- $\text{Mg}(\text{OH})_2$  nanocomposites are HB and V-0 respectively. The

results show that the  $Mg(OH)_2$  nanostructure can enhance the flame retardant property of the PVA matrix. In the presence of flame nanoparticles build a barrier, this barrier slows down evaporation of polymeric segments and prevents reaching oxygen and flame to the sample. Samples of PVA- $Mg(OH)_2$  nanocomposites under UL-94 test are shown in Fig 10.

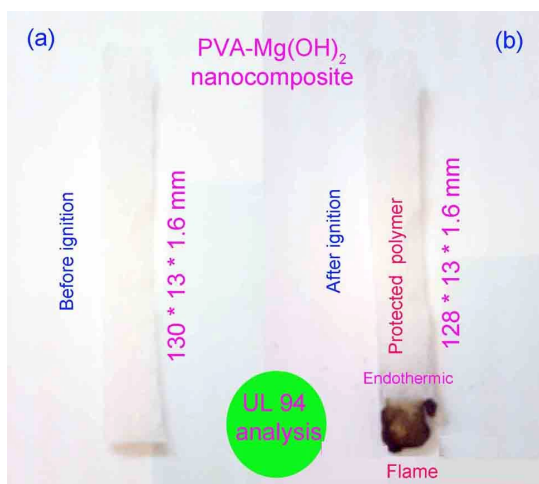


Fig. 10. Performance of nanocomposite under UL-94 test

#### 4. Conclusion

$Mg(OH)_2$  nanostructures were prepared by a rapid microwave method. The effect of various surfactants such as SDS, CTAB and PEG on the morphology of magnesium hydroxide nanostructures was investigated.  $Mg(OH)_2$  nanoparticles were then added to poly vinyl alcohol matrix. The influence of the inorganic phase on the thermal properties of polymer matrixes was studied using thermo-gravimetric analysis and differential thermal analysis. Thermal decomposition of the PVA nanocomposite shift towards higher temperature in the presence of  $Mg(OH)_2$  nanoparticles. The enhancement of thermal properties of the nanocomposites is due to endothermic decomposition of  $Mg(OH)_2$  and release of water which dilutes combustible gases.  $Mg(OH)_2$  have also barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer.

#### Acknowledgements

The authors gratefully acknowledged the financial and other support of this research, provided by the Islamic Azad University, Yadegar- e-Imam Khomeini (RAH) Shahr-e-Rey Branch, Tehran, Iran.

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