

# INVESTIGATION OF THE MODIFICATION PROCESS AND MORPHOLOGY OF ORGANOSILANE MODIFIED NANOCCLAY

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*This work deals with the preparation of epoxy-clay nanocomposites. The results show that the mechanical properties of nanocomposites depend on their compatibility, the epoxy resin used and the purity of the nanoclay. The used bentonite was purified and the effects of the organoclay synthesis and various additives on its characteristics were evaluated. X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM) were used to analyze the microstructure and the phase composition of the nanoclay. The XRD results revealed that when the modifier addition was increased from 10 wt.% to 40 wt.%, the interlayer spacing of the nanoclay increased from 12.43 Å being incompatible with the resin to 20.43 Å making possible to prepare required nanocomposite.*

## INTRODUCTION

The use of compounds that contain a polymer base that has been amended with a solid substance to improve its characteristics has been conducted for a long time. However, to improve the properties of the polymer, the type and structural characteristics of the fillers used must be carefully considered. This is because the interaction of particles in these compounds and their effects on the formation of aggregates within the polymer matrix determines the mechanical, thermal and viscoelastic properties of the system. Therefore, it is essential that the surface energy of the filler and the chemical characteristics as well as the matrix viscosity of the polymer be studied thoroughly. Because it is important to select a suitable filler to ensure the desired properties are obtained; sufficient attention should be paid to effective and key factors such as the size, shape and size distribution of the particles, as well as the dispersion and adhesion between the polymer and filler in the system. Recent studies have indicated that the number of suitable fillers is rapidly increasing. However, when developing a composite, the aforementioned parameters, as well as the fillers used, their cost and possible pollution by their production should be carefully considered [1].

The results of studies conducted to evaluate new materials over the last few decades have shown that changing the combination and structure of substances

at the nanometer scale can lead to the development of new composites with unique characteristics. The majority of recently conducted studies have focused on synthesizing nanomaterials and nanocomposites and improving their properties. It has been predicted that the annual consumption of nanocomposites will grow by more than 20 percent worldwide, which further emphasizes the need for new materials of this type. Due to the wide availability, high aspect ratio and suitable price of clay minerals, these materials are widely used for the production of polymer nanocomposites [2]. Nanocomposites produced based on layered silicates such as montmorillonite are of great importance due to their characteristics. Montmorillonite is comprised of many overlapping layers of crystal particles that generally have an average thickness of 0.96 nm and a diameter of 100-200 nm [3] (Figure 1). However, due to the hydrophilic nature and high moisture absorption of clay, it is very difficult to produce polymer nanocomposites from clay and polymers with an exfoliated clay structure. Because it is necessary to establish a suitable bond between clay particles and the matrix to produce a composite with desirable properties, it is necessary to modify the clay with organic materials. Several studies have described the purification of clay [4, 5]. For example, Bazzgir et al [3] showed that physical methods, such as the use of a Hydrocyclon, can effectively remove most impurities from clay. In this study, we found that the most effective

method of producing polymer composites with exfoliated structure, clay was to increase the interlayer spacing in as few steps as possible (Figure 2). When using this strategy, the initial inflation of montmorillonite in water may increase the interlayer spacing from 0.96 nm to 1.3 nm. However, during the second stage, the infiltration layers by molecules compatible with organic materials or intercalation eventually causes the interlayer spacing to reach more than 2 nm. In the third stage, penetration of the layers into the polymer chain causes the opening of more layers, and under optimal conditions, complete exfoliation of the clay plains in the polymer base. Many organic materials have been used in such processes, and these materials have primarily been based on commercial grade alkyl ammonium compounds [6-14]. Using ammonium alkyl compounds, particularly those with a more organic nature, lowers the possibility of intercalation of the clay layers. However, the organic and polar nature

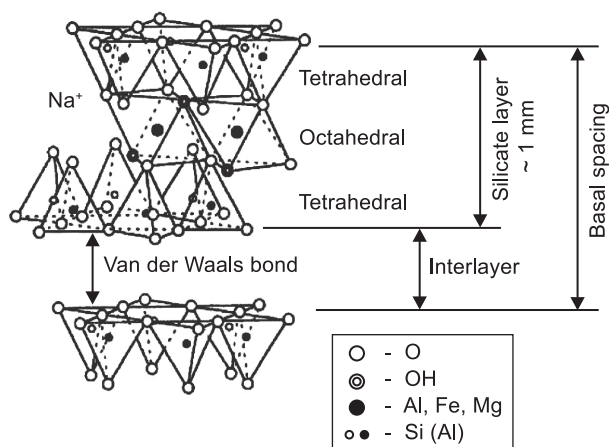


Figure 1. Layer structure of montmorillonite [3].

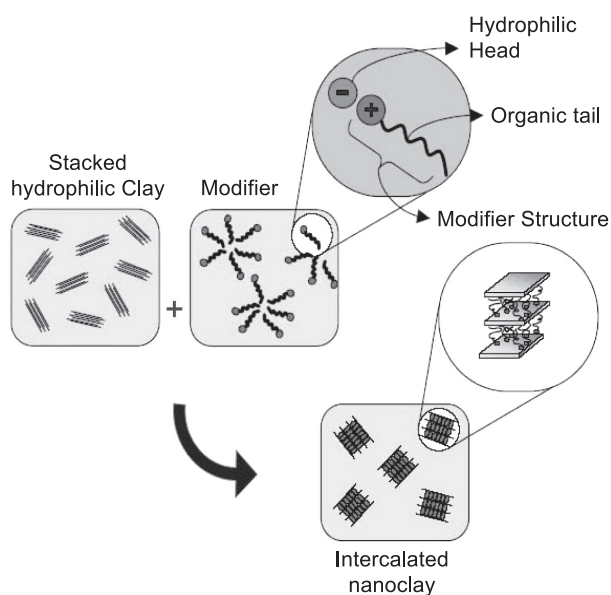


Figure 2. Clay modification process.

of silanes causes them to react with nanoclays on one end and with the polymer on the other, thereby allowing binding to occur. In spite of this, few reports have been conducted to evaluate the use of silanes in composites [15, 16].

## EXPERIMENTAL

Local sodium bentonite with a mesh size of 200 and a particle size that was less than 75  $\mu\text{m}$  was used in this study. The bentonite was produced by a powder company (Poodrsazan, Tehran, Iran) and amended with the chemicals shown in Table 1. A suitable Gamma-3-aminopropyltrimethoxy silane obtained from Sigma Aldrich was used to modify the clay. An Oxford-ED2000 XRF was used for all chemical analyses.

Table 1. Chemical composition of bentonite.

Formula	wt. %
L.O.I	13.2
Na <sub>2</sub> O	2.04
MgO	2.22
Al <sub>2</sub> O <sub>3</sub>	14.59
SiO <sub>2</sub>	61.03
SO <sub>2</sub>	0.37
Cl	0.46
K <sub>2</sub> O	0.76
CaO	0.77
TiO <sub>2</sub>	0.22
Fe <sub>2</sub> O <sub>3</sub>	2.09
BaO	0.11

Following preparation and analysis of the raw materials, the clay was purified using a 2-inch hydrocyclone apparatus. To accomplish this, a suspension of 3 wt.% clay in distilled water was prepared and then passed through the cyclone at a pressure of 0.15 MPa. This resulted in the removal of impure and large particles. Montmorillonite particles with a diameter of less than 6  $\mu\text{s}$  were then dried and used in the compatibility process. To ensure compatibility following the dispersion of clay in distilled water, a suspension comprised of clay was prepared and amended with 10, 20, 30, 40 or 50 (wt.%) percent of the modifier materials „silane“. The mixtures were then heated at 80°C for 6 hours, after which the products were washed with distilled water and dried. The distribution of clay particle sizes was measured before and after purification using a Laser Particle Size Analyzer (Fritsch, LPSA, Germany). In addition, clay particles in the colloid state were analyzed by SEM, (Model LEO 440, England). The intercalation of the samples was evaluated using an X-ray diffraction (XRD) system, Brocker, Germany).

RESULTS AND DISCUSSION

As shown in Figure 3 and Figure 4, most of the particles in the clay are in the agglomerated form prior to purification. In addition, all of the particles in the clay had diameters of less than 75  $\mu\text{m}$ . Furthermore, 50 %

of the particles in the clay were less than 7  $\mu\text{m}$  and 80 % were less than 20  $\mu\text{m}$  in diameter. Since particles greater than 5  $\mu\text{m}$  in diameter prevent the formation of a suitable product, it was necessary to employ a purification method to remove these particles.

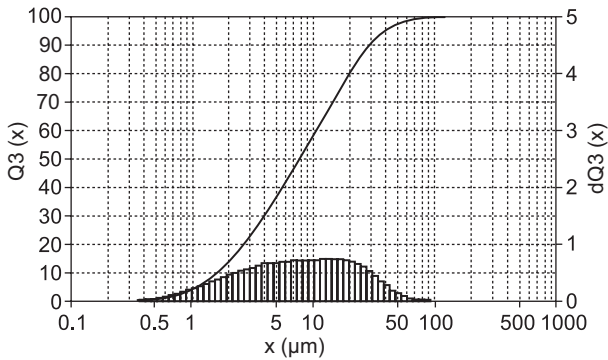


Figure 3. Diagram of accumulative distribution of clay particles in feed before purification.

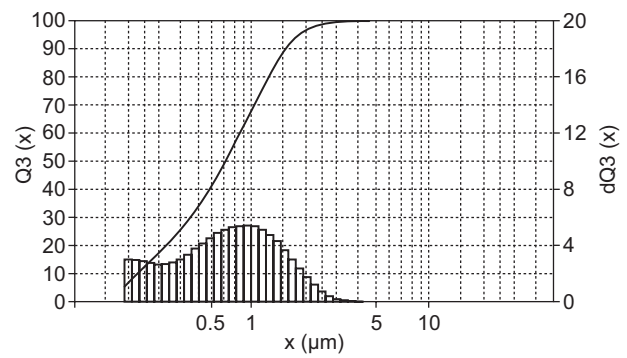


Figure 6. Diagram of accumulative distribution of clay particles in feed after purification.

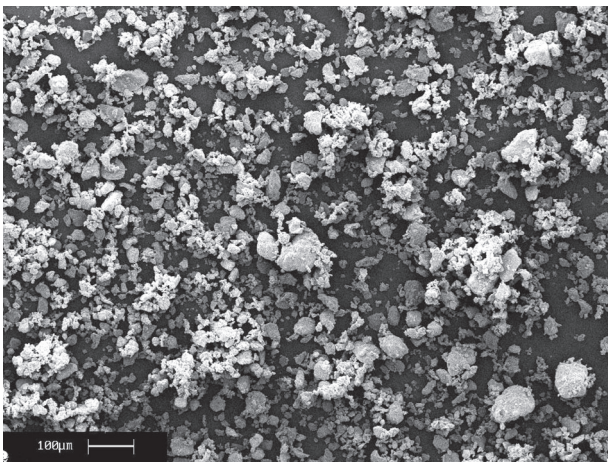


Figure 4. SEM image of clay particles in feed before purification.

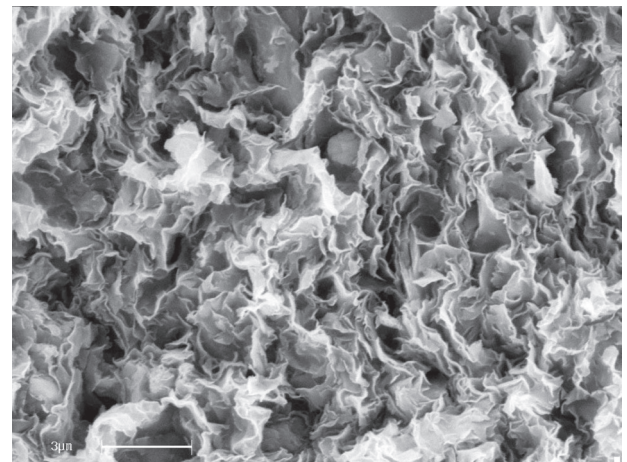


Figure 7. SEM image of pure clay in magnetite.

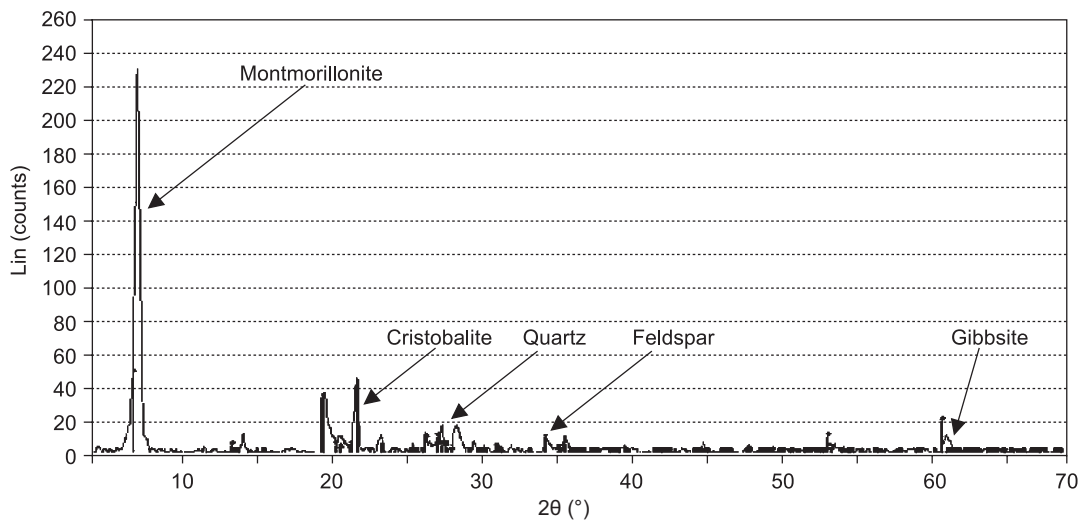


Figure 5. XRD pattern, local pure sample.

The results of the XRD analysis revealed that most of the impurities, which included quartz, cristobalite, calcite, gibbsite and feldspar, were removed from the clay by the purification process (Figure 5). In addition, analysis of the particle size distribution (Figure 6) revealed that most of the particles were less than 5  $\mu\text{m}$  in diameter and that greater than 80 percent of the particles

were less than 2  $\mu\text{m}$  in diameter following purification. Finally, the thickness of the layers in the crystal structure of montmorillonite and the patterns generated by XRD indicate that the clay was comprised of crystal layers on top of each other following purification (Figure 7).

It is well known that replacing the Al in montmorillonite with Mg induces a negative load in crystals,

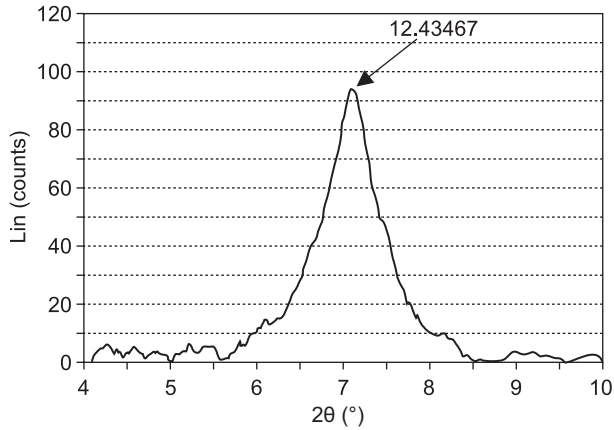


Figure 8. XRD pattern, pure and unmodified internal sample.

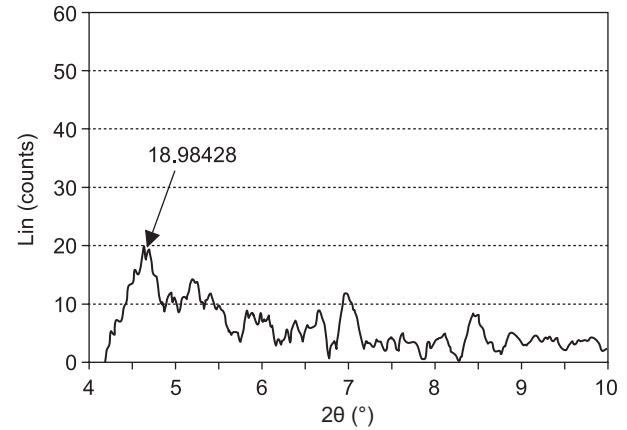


Figure 11. XRD pattern of the sample modified by the addition 30 wt.% of silane.

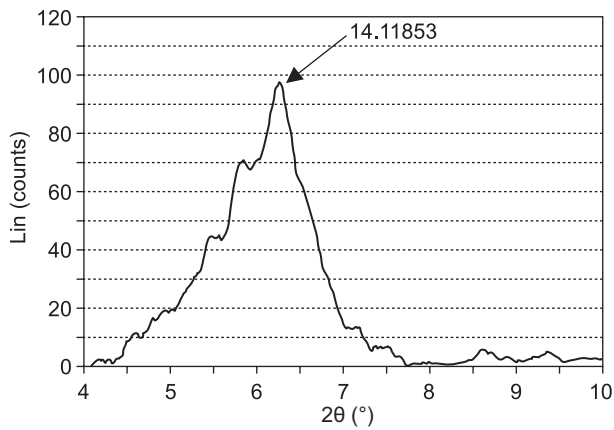


Figure 9. XRD pattern of the sample modified by the addition 10 wt.% of silane.

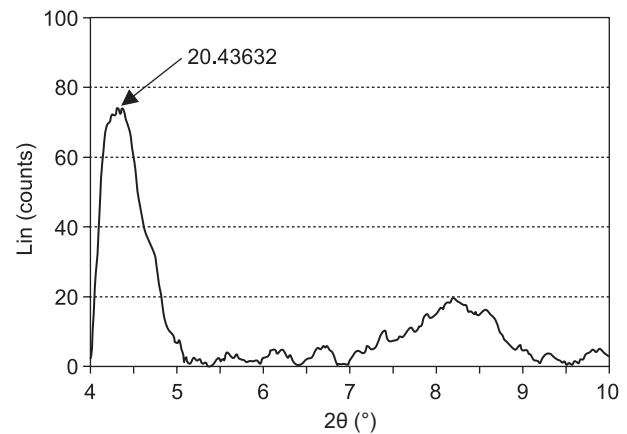


Figure 12. XRD pattern of the sample modified by the addition 40 wt.% of silane.

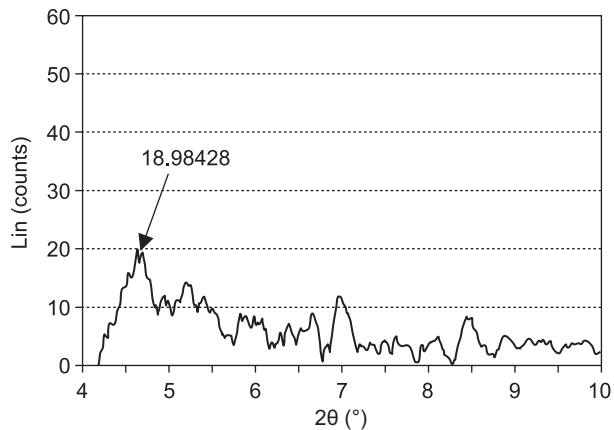


Figure 10. XRD pattern of the sample modified by the addition 20 wt.% of silane.

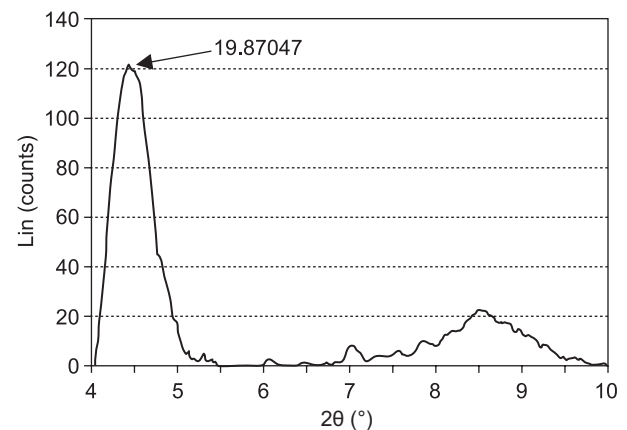


Figure 13. XRD pattern of the sample modified by the addition 50 wt.% of silane.

and that this negative load can be neutralized with sodium ions or similar ions [13]. Therefore, the number of positive ions in the structure of this mineral affects its properties, particularly the degree of ionic exchange that occurs with polymers during the modification and compatibility process. As shown in Figure 6, during the modification process, the organic compounds are placed between the clay layers, which results in the interlayer spacing increasing. One of the most important methods for studying the interlayer spacing is X-ray diffraction (XRD), and the 001 montmorillonite mineral peak displacements at  $2\theta$  is a suitable criterion to evaluate the interlayer spacing. Specifically, a decrease in the  $2\theta$  angle indicates an increase in interlayer spacing [13].

The XRD spectrum of the purified sample at  $2\theta$  between 4 and 10 degree is shown in Figure 8. This figure clearly indicates that the strong peak corresponding to the 001 montmorillonite mineral in the  $2\theta$  position is approximately 7 degree while, the interlayer spacing in the unmodified clay is approximately 12.5 Å [17]. As was expected, this value varied and increased as modifiers were placed between the layers. This effect shows that the increase in interlayer spacing is highly dependant on the amount of modifier used. As shown in

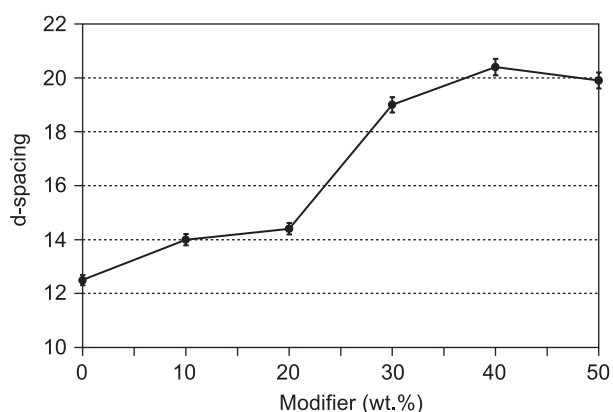


Figure 14. Diagram of interlayer spacing vs. the content of the modifier.

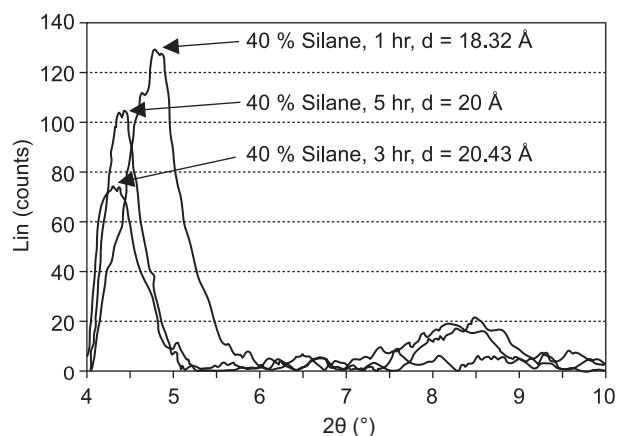


Figure 15. XRD pattern of the sample modified by the addition 40 wt.% of silane in 1, 3 and 5 hours.

the XRD spectra of the modified clay samples (Figures 9 to 13), increasing the amount of modifier from 10 to 40 percent resulted in increased spacing of the interlayers. However, when the modifier amount was increased from 40 percent to 50 percent, little additional increase in spacing was observed. This indicates that the interlayer spacing increased from 12.43 Å to 20.43 Å in response to modification. Based on these results, 40 wt.% silane was selected as the optimum amount of filler for the modification process (Figure 14). Next, the reaction time was evaluated. The modification process was conducted using 40 wt.% silane and allowed to run for 1, 3 and 5 hours. As shown in Figure 15, the modification process induced little effect on interlayer spacing after 1 hour, but the maximum interlayer spacing (20.43 Å) was obtained after 3 hours. Furthermore, no further increase in spacing was observed when the process was allowed to run for 5 hours. Taken together, these results indicate that the optimal time for the modification process was 3 hours.

## CONCLUSIONS

The results showed that domestic clay can be used in the formulation of nanocomposites after applying a suitable purification and modification process. The size distribution of the purified samples revealed that the separation process removed all particles greater than 5 microns in diameter. Furthermore, more than 70% of the particles that remained after separation were less than 1 µm in diameter.

The interlayer spacing of the unmodified sample was 12.43 Å being incompatible with the resin. The treatment procedure resulted in an increased value 20.43 Å being suitable for the nanocomposite preparation. The addition 40 wt.% of silane was determined to be the optimal amount of additive. The optimal time for the modification process is 3 hours. The layered structure of the final samples was determined by the SEM technique.

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