

## Influence of Modes Shredding of Source Components by Processes to Synthesis and Activity of Powder Sintering Hexaferrite

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The influence of the modes of wet grinding of the original ferrite-forming components on their activity and the temperature of the synthesis powders of hexaferrites. It is shown that grinding of the initial components in the acidic environment can reduce the synthesis temperature of hexaferrites. The increased activity of the powders during milling in acidic medium due to the formation on the surface of particles of gel-like layers of hydroxides of barium or strontium. The activity formed gelled layers to a significant extent can be controlled by introducing surfactants in the wet grinding.

**Keywords:** Hexaferrite, Synthesis, The acidic environment, Wet grinding, Interlayers.

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### 1. INTRODUCTION

The activity of hexaferrites powders to be sintered has a significant impact on the density of the sintered ferrite substrates. In this regard, it is critical to develop ways of regulation of activity of the powders to be sintered. It is known [1, 2] that such activity of powders of hexaferrites is very substantially determined by the temperature of synthesis of these compounds from the source components and the activity of original components. However, the process of wet grinding of the synthesized powders of hexaferrites can have a significant impact on their activity to the sintering. This is due to the large content of alkaline earth metals barium and strontium hexaferrites in that the wet grinding process is partly dissolved in an aqueous medium with subsequent formation of an active gelled layers on the particle surface. The activity of these layers is not stable enough, which reduces the reproducibility of the properties of the resulting hexaferrites.

The research work carried out in order to increase the activity of hexaferrite powders by increasing the thickness of the heat-resistant gel-like layers on the surface of the particles that can annihilate slowly at temperatures of sintering shrinkage and activate.

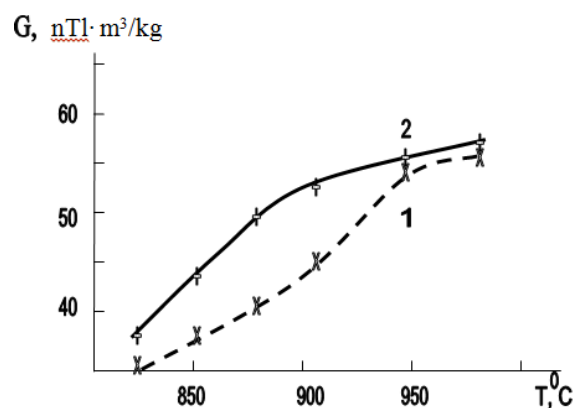
### 2. RESULTS AND DISCUSSION

Powders of hexaferrites were obtained by mixing barium carbonate BaCO<sub>3</sub> GOST 2149-75 "analytical grade" or strontium SrCO<sub>3</sub> TO-2326-91 "analytical grade" with iron oxide Fe<sub>2</sub>O<sub>3</sub> TU6-09-4783-83 "MM-1" in the conical mixer. The resulting mixture was ground in a vibrating mill M-10 dry and wet process for 2 hours and calcined in a furnace with rotating tube "Hyperbole" at a temperature of 800-10000 °C. The residence time of the charge in the zone with the maximum temperature in the furnace was 3 hours. The charge is synthesized in all the experimental batches were wet milled in the attritor are considered "Ararat" for 2 hours with addition of water and 0.2 wt% citrate of triethanolamine.

From the suspension after wet grinding of the workpiece is extruded in the form of plates 20 × 40 × 5 mm in a magnetic field with a strength of 700 kA/m at the press O6FFG. After drying the billet was sintered in tunnel kiln "Spruce" in the temperature range from 800 to 1200 °C.

With the aim of increasing the activity of the mixture of initial components for the synthesis of ferrite powders in their grinding used surface-active substances (surfactants): isopropyl alcohol, citric acid, triethanolamine. Figures 1-4 shows data on the effect of method of grinding and SAS on the specific magnetization of the synthesized hexaferrites powders at different synthesis temperatures.

As can be seen from the data shown in the figures, the maximum values of specific magnetization of the synthesized charge, i.e. the highest activity to the synthesis, is provided by wet grinding in an acidic environment, which is formed when additives of isopropyl alcohol and citric acid.



**Fig. 1** – Influence of surfactants in dry milling and synthesis temperature of the charge at the specific magnetization of the charge of barium hexaferrite: 1 – without SAS; 2 – 0.3 wt % of the triethanolamine

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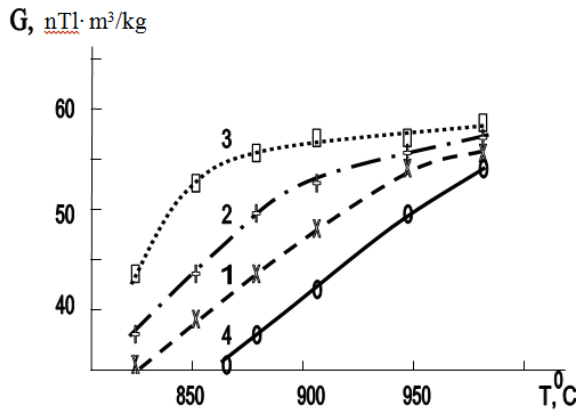


Fig. 2 – Influence of SAS during wet grinding, and the synthesis temperature of the charge at the specific magnetization of the charge of barium hexaferrite: 1 – without SAS; 2 – 0.5 wt % of the isopropyl alcohol; 3 – 0.2 wt % of the citric acid; 4 – 0.3 wt% of the triethanolamine

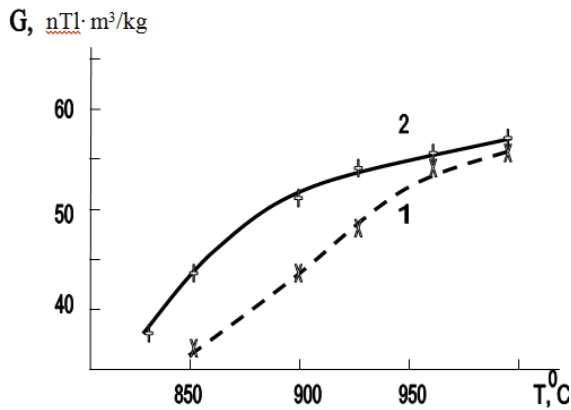


Fig. 3 – Influence of SAS in dry milling and synthesis temperature of the charge at the specific magnetization of the charge strontium hexaferrite: 1 – without SAS; 2 – 0.3 wt % of the triethanolamine

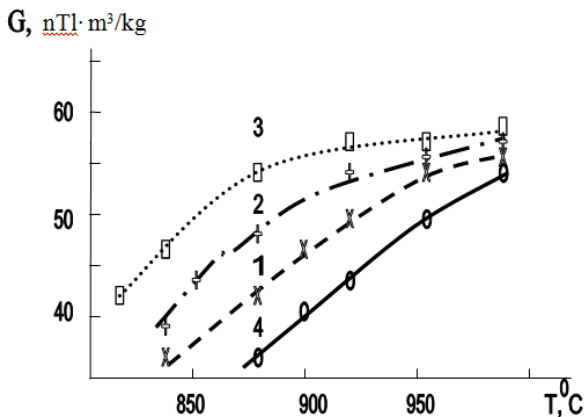


Fig. 4 – Influence of SAS during wet grinding, and the synthesis temperature of the charge at the specific magnetization of the charge strontium hexaferrite: 1 – without SAS; 2 – 0.5 wt % of the isopropyl alcohol; 3 – 0.2 wt % of the citric acid; 4 – 0.3 wt % of the triethanolamine

This can be explained by decomposition of the carbonates of barium and strontium under the action of acid, followed by dissolution of the hydroxides of barium and strontium in water. During subsequent drying the

hydroxides deposited on the surface of iron oxide particles, forming a gel-like active layer. In neutral and alkaline medium formed by adding triethanolamine, the solubility of hydroxides of barium and strontium is reduced, which also reduces the activity of the powders after grinding. Dry grinding offers a lower activity of powders synthesis as compared with wet grinding. Generally, wet grinding of the starting components in an acidic environment can reduce the synthesis temperature of hexaferrites at 30-500 °C.

Studies have shown that wet grinding in an acidic environment can reduce not only the temperature of the synthesis mixture, and the sintering temperature of the raw press blanks at 40-600 °C (Fig. 5 and 6). As can be seen from the data shown in the figures, the maximum density values of sintered workpieces is also ensured in the wet grinding of the starting components in the acidic environment formed when additives of isopropyl alcohol and citric acid. This can be attributed to activity of powders and after the operation of synthesis of the charge.

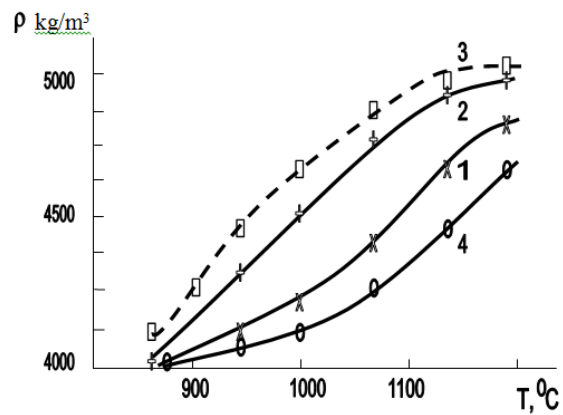


Fig. 5 – Effect of sintering temperature and nature of the SAS during wet grinding of a mixture of the initial components of the density of the billets of Ba-ferrite: 1 – without SAS; 2 – 0.5 wt % of the isopropyl alcohol; 3 – 0.2 wt % of the citric acid; 4 – 0.3 wt % of the triethanolamine

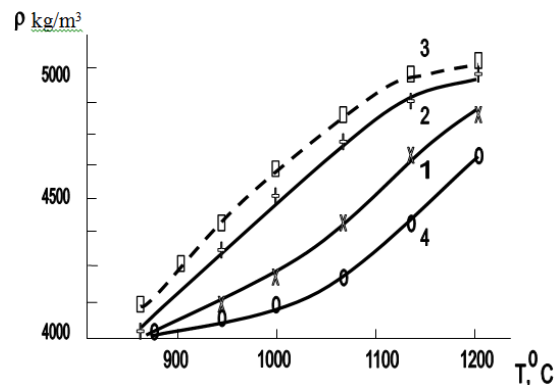


Fig. 6 – Influence of the sintering temperature and the nature of the SAS during wet grinding of a mixture of the initial components of the density of the blanks of Sr-ferrite: 1 – without SAS; 2 – 0.5 wt % of the isopropyl alcohol; 3 – 0.2 wt % of the citric acid; 4 – 0.3 wt % of the triethanolamine

With the aim of increasing the reproducibility of the technological properties of powders and molding compounds were used for additional chemical modification

of the surface of the particles of hexaferrites in the aquatic environment. The modification consisted in the precipitation of hydroxides of the cations on the particle surface produced by wet milling of powders with additions of polyelectrolytes and their subsequent drying. Studies have shown that the gel layer of the chemical composition is amphoteric the hydroxide Hydrosol whose density largely depends on the pH of the medium during grinding and subsequent drying. It was found that the deviations from the neutral pH causes increased dissolution of the gel-like layer, accompanied by its swelling and changes in the rheological properties of suspensions.

Studies have shown that the processes of dissolution of ions from the surface of the hexaferrite in the aquatic environment and subsequent deposition on the surface of the polymer chains of these ions in the form of oxides or hydroxides, causing the spontaneous modification of the surface properties. Gel-like layer on the surface of the particles formed as a result of these processes, characterized by high activity due to the excess free energy, significantly activates the process of mass transfer at the initial stage of sintering.

Fig. 7 shows the effect of the duration of the wet milling ferrite charge on the temperature of the beginning of the shrinkage of ferrite pieces when heated by sintering at a speed of 150 °C/h. Ba-ferrites have a higher value of point of zero charge (PZC) than Sr-ferrites (8.7 and 8.4 respectively), which explains the stronger dependence of the activity of gel-like layers from the time of grinding.

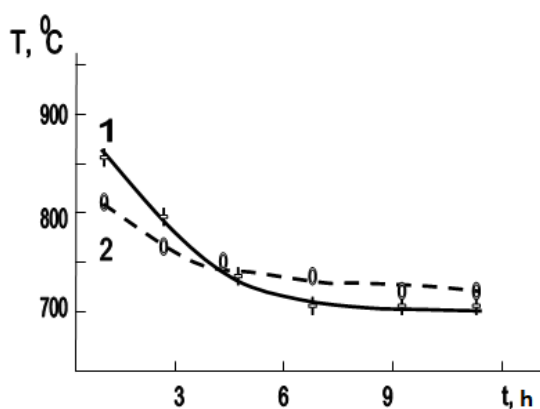


Fig. 7 – Effect of length of wet milling ferrite charge on the shrinkage start temperature preforms Ba (1) and Sr (2) under heating in ferrite sintering

Experiments showed that the polyelectrolyte significantly affect the process of dissolution of ions from the surface of hexaferrite and activity gelatinous layers. It is established that in the absence of polyelectrolytes, the rate of dissolution of ions decreases exponentially with time according to displacement of the pH of the aqueous environment from a neutral point to the value PZC. Polyelectrolytes possess buffering capacity and is capable of long time to maintain the setpoint pH in the aquatic environment, ensuring the constancy of the speed of dissolution of ions from the surface of particles of ferrite.

It is established that the introduction of a polyacid in the suspension of powders of hexaferrites creates an

acidic environment that increases the rate of diffusion of cations of alkaline-earth metals barium and strontium from the surface of the ferrite in aqueous medium. As a result of increasing ion concentration of barium and strontium in solution, and thereby, the thickness of the gel layer formed from these ions due to their precipitation on the surface of the particles during the drying process of suspensions and the preparation of moulding masses.

Studies have shown that the presence of an excess of gel-like layers on the surface of particles is often undesirable because it significantly affects the rheological properties of suspensions and molding compounds due to the increase in interparticle friction and cohesion. In addition, excessive activity of the surface layers causes zonal isolation during subsequent sintering of powders, which significantly reduces the density and quality of the ferrite.

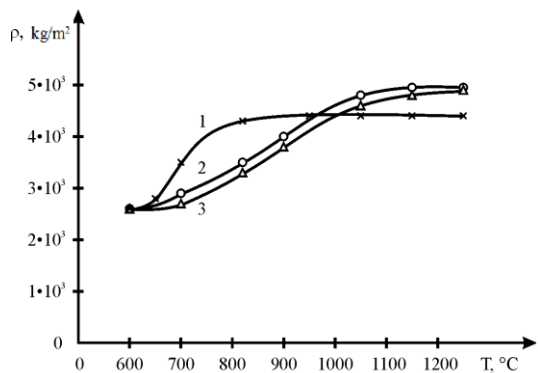
The activity of the resulting gel layers strongly depends on the magnitude of change and rate of change of pH during the chemical modification of the surface. Smooth change in pH upon administration to a suspension of alkali to precipitate the cationic polymer chains or by the introduction of anionic acid to precipitate the polymer chains, allows obtaining a denser and less active gel layer. Rapid change in pH causes an intense deposition of polymer chains with the formation of loose, but very active gel layers.

To adjust the activity of gel-like layers applied to the heat-treated powders after wet grinding in the temperature range of 400...800 °C. Good results on stabilization activity were achieved by the introduction of inactivators in the wet milling of powders. As the inactivators were used fine powders of CaCO<sub>3</sub> and CaSiO<sub>3</sub> able in a large number of adsorbing polymer chains with the formation of a dense, moderately active gel layers. Carbonates and silicates probably form complicated complexes with the polymer chains, smoothing the activity of a gel interlayer and a smooth shrinkage. On the other hand, on the surface of particles of carbonates and silicates there are germinal centers that form a dense precipitation of the hydroxides of barium and strontium from the suspension.

Found that long time exposure of workpieces to air before sintering also contributes to the smoothing activity of gel-like layers. However, more reasonable results are obtained in the drying process at 200-600 °C the drying Temperature should be high so as not began the process of diffusion of the particle slip and sintering, but is sufficient to smooth the gel-like active layers.

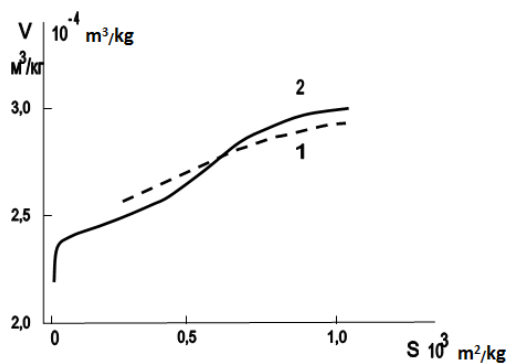
Fig. 8 shows the effect of inactivators on the kinetics of sintering of blanks of Sr-ferrite powders during heating under sintering. As can be seen from the data supplements provide more uniform shrinkage and high density sintered products. Blanks without inactivator characterized by their high activity at the initial stage of sintering, which is the cause of zonal isolation, which does not allow to achieve high density.

The choice of composition and amount of SAS to activate the sintering depends on many factors: the chemical composition of oxide ceramics, the dispersion of particles of modes of sintering, etc. So the choice of composition and amount of SAS in specific technologies ferrite products is carried out experimentally.

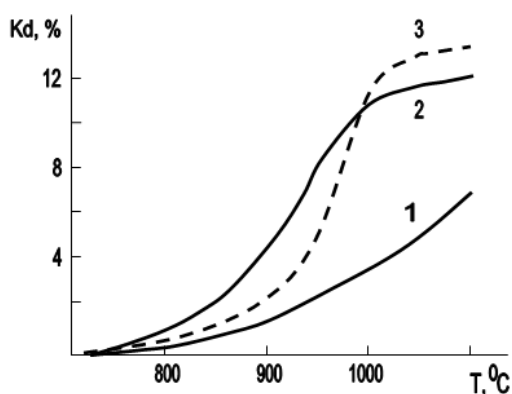


**Fig. 8** – Dependence of the density of blanks SrFe<sub>12</sub>O<sub>19</sub> temperature under heating for sintering at 100 °C/h: 1 – without additives; 2 – 0.5 wt % of CaCO<sub>3</sub>; 3 – 0.5 wt % of CaSiO<sub>3</sub>

Studies have shown that the mass transfer is intensified gelatinous veins mainly at the initial stage of sintering. This is confirmed by a sharp decrease in the free surface active workpieces and shrinkage (Fig. 9 and 10). It is established that, with appropriate surface modification of the particles, the main transport mechanism of the mass transfer consists in the sliding of the particles as one-piece units along the surfaces between them.



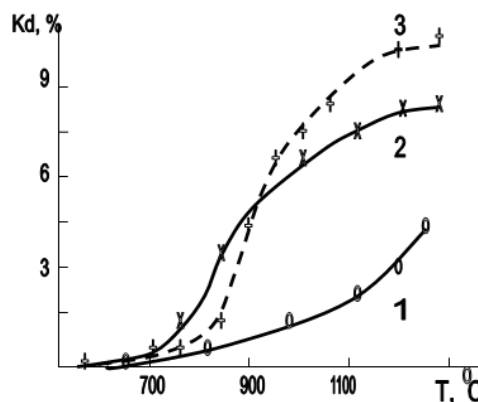
**Fig. 9** – Influence of gel layers on the dependence of the specific volume of the billet Ba-ferrite when heated to 1100 °C at a speed of 100 °C/h from the free surface of the workpiece: 1 – piece with no of layers; 2 – layers



**Fig. 10** – Influence of gel layers on the kinetics of shrinkage of billets of Ba-ferrite: 1 – the material without layers; 2 – with layers; 3 – with layers and 0.5 wt % CaCO<sub>3</sub>

The moving particle can be rotated around their centers. In this sense, the mechanism of shrinkage of such viscous fluid flow, where the peculiar role of the "molecules" are particles of a raw. Therefore, strong shape dispersion system at a high temperature becomes liquid-like. The temperature of "melting" depends on the chemical composition of the ferrite, the dispersion of particles and activity of gel-like layers.

Studies have confirmed that the activity of gel-like layers on the surface of ferrite particles largely depends on the rate of deposition of polymer chains. Gel-like layer, characterized by porosity and unstable activity, mainly formed by the rapid drying suspensions and slurries at high temperatures (80-100 °C) during spray drying of suspensions, causing rapid sedimentation of the polymer chains on the particle surface (Fig. 11).



**Fig. 11** – Influence of gel layers on the kinetics of shrinkage of billets of Sr-ferrite: 1 – the material without layers; 2 – with layers; 3 – with layers and 0.5 wt % CaCO<sub>3</sub>

In the sintering process is the reduction in the activity of a gel interlayer and a gradual decrease in the rate of sintering. An important task in the technology of high-density ferrites is the high activity of particles at the intermediate stage of sintering because at the intermediate stage of sintering is the main seal of the workpiece.

It is shown that at the intermediate stage of sintering of high activity exhibit a more dense gel layer that is less active in the initial stage of sintering, but is able to smoothly reduce their activity during sintering. But, studies have shown a smooth change of activity for sintering additives have carbonates. This can be explained by their decomposition during sintering and carbon dioxide. Carbon dioxide is able to exert an oxidizing effect on the gel layer and to reduce their activity.

Developed methods of formation of gel-like active layers on the particle surface has allowed to lower the sintering temperature of hexaferrites by 50-100 °C (Tables 1 and 2) sintering energy consumption by 10-15 %. Grinding of defective products in the aquatic environment with the addition of polyelectrolytes allows to obtain the active powder, able to be sintered at relatively low temperatures. Reducing the sintering temperature and processing of defective products allowed on 15-20 % lower cost ferrite products.

**Table 1** – Influence of the sintering temperature and activation of powders on the density and properties of barium hexaferrites

Sintering temperature, °C	Modification of particle	$\rho$ , kg/m <sup>3</sup>	$B_r$ , T at 25°C	$H_{cb}$ , kA/m	$H_{cl}$ , kA/m	$W$ , kJ/m <sup>3</sup>
1010	No	4,1	0,21	170	213	8
	Yes	4,7	0,38	214	229	13
1030	No	4,4	0,31	185	217	10
	Yes	4,8	0,40	216	234	14
1050	No	4,6	0,37	190	219	11
	Yes	4,8	0,42	216	239	14
1070	No	4,7	0,38	190	223	13
	Yes	4,9	0,42	218	234	14
1090	No	4,8	0,39	201	221	13
	Yes	4,9	0,42	216	231	14
1110	No	4,8	0,41	211	220	14
	Yes	4,8	0,40	211	230	13

**Table 2** – Effect of sintering temperature and activation of powders on the density and properties of strontium hexaferrites

Sintering temperature, °C	Modification of particle	$\rho$ , kg/m <sup>3</sup>	$B_r$ , T at 25°C	$H_{cb}$ , kA/m	$H_{cl}$ , kA/m	$W$ , kJ/m <sup>3</sup>
1050	No	4,0	0,19	175	233	7
	Yes	4,7	0,38	214	249	13
1070	No	4,3	0,30	189	237	9
	Yes	4,8	0,40	219	254	14
1090	No	4,6	0,36	197	239	11
	Yes	4,8	0,42	226	259	14
1110	No	4,7	0,38	199	243	13
	Yes	4,9	0,42	228	254	14
1130	No	4,8	0,39	208	251	13
	Yes	4,9	0,42	226	251	14
1150	No	4,8	0,41	221	250	14
	Yes	4,8	0,40	214	231	13

### 3. CONCLUSION

Found that wet grinding of the starting components in an acidic environment can reduce the synthesis temperature of hexaferrites at 30-50 °C. The increased activity of the powders during milling in acidic medium due to the formation on the surface of particles of gel-like layers of hydroxides of barium or strontium.

Found that wet grinding the synthesized mixture of barium hexaferrites and strontium with the introduction of the polyelectrolyte promotes the formation of gel-like active layers on the surface of particles of ferrite. It is shown that the activity of gel-like layers strongly depends on the rate of their deposition on the particle surface during drying of suspensions. Excessive activity is the cause of inter-layer zonal isolation and the formation of cracks at the initial stage of sintering by heating of the ferrite blanks for sintering. Smooth change of pH before drying the suspension allows to precipitate on the surface of the

particles more dense and less active in the initial stage of sintering the gel layer.

Positive results on stabilization of activity of the powders obtained by the introduction of a suspension of carbonates and silicates. Developed methods of formation of gel-like active layers on the particle surface has allowed to lower the sintering temperature of ferrites on the 50-1000 °C. The thus-obtained barium hexaferrites and strontium (as a nominally pure chemical composition and with different substitutions in the iron sublattice) meet all of the criteria when used as a permanent magnet, and as substrates subminiature microstrip ferrite decoupling devices shortwave part of the millimeter wavelength range.

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