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EFFECT OF CURING ON THE PERFORMANCE OF LEAD-ACID BATTERY POSITIVE PLATES

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ABSTRACT. The performance of a lead-acid battery depends on the structure and composition of positive active mass, a mixture of α-PbO_2 and β-PbO_2. The amounts of these two crystal PbO_2 modifications that are formed in the positive active mass depend on the processing plate history and on its formation conditions. The curing process is the longest step in the manufacture of lead-acid batteries. In this work the effect of three different curing methods on the physico-chemical and electrochemical properties of positive plates was studied. IR spectra, X-ray diffraction, scanning electron microscope observations and wet-chemical analysis were used as techniques of investigation. It has been observed that curing conditions (duration, humidity and temperature) strongly influence electrode phase-composition and electrical performance. A continuous recrystallization process and a growth of crystal size were observed during curing at low temperature and inadequate humidity and temperature.

INTRODUCTION

It is generally accepted that a good automotive lead-battery should have both high initial and reserve capacity and long deep-discharge cycle life [1-3]. In a major part, this performance depends on the structure and composition of positive active mass, which consists of a mixture of two PbO_2 crystal modifications: α-PbO_2 (orthorhombic) and β-PbO_2 (tetragonal) [4-7]. The amounts of α-PbO_2 (formed in a neutral or alkaline environment) and β-PbO_2 (formed in an acidic environment) in the positive active mass depend on the processing plate history (leady oxide preparation, mixing and curing of positive materials) and of the plates formation conditions (sulfuric acid concentration, time of soaking, charge current density and temperature) [8-10].

Applying a paste of "leady oxide", water and diluted sulfuric acid onto a lead or lead-alloy grid structure produces the positive plates.

The "leady-oxide" usually comprises about three-part lead monoxide (α-PbO and β-PbO) to one-part fine lead particles (so-called "free lead") [3]. Sometimes, the oxide is blended with a minor percentage of red lead (Pb_3O_4) as well as with certain proprietary additives that are thought to benefit the manufacturing procedure and/or battery performance.

From the steps involved in the positive plate manufacturing process, curing is a key stage, while the paste is converted into a cohesive, porous mass, with a good adherence to the grid. Poor control of the process will diminish the mechanical strength and the electrical performance of the plates during battery service life [11]. The transformations that take place during the curing are dependent on the composition of starting materials and processes which occurs in the mixing and pasting steps [12-16].

It has been established that the following processes, either separately or simultaneously, occurs during the curing of pasts [1,2,4,11,16]:

- oxidation of free lead particles to lead monoxide with liberation of heat;
- conversion of lead monoxide to mono, three or tetra - basic lead sulfates ($PbO \cdot PbSO_4$-1BS; 3 $PbO \cdot PbSO_4 \cdot H_2O$-3BS; 4 $PbO \cdot PbSO_4$-4BS);
- recrystallization and interconversion of basic lead sulfates;
- development, of basic lead carbonate ($2.PbCO_3.Pb(OH)_2$ - HC) on the surface of the plate;
- corrosive attack of the metallic grids;
- evaporation of water from plates.

It has been found that the positive active mass obtained from 3BS rich paste contains small PbO_2 crystals. Due to their high surface area they assure a high initial capacity, being appropriate to the manufacture of automotive batteries [2,11]. The plates formed from 4BS rich paste have a lower capacity and an inferior charge acceptance, but a longer cycle life and could be used for industrial batteries [7,13-16].

The relative amounts of 3BS and 4BS in the positive paste are influenced by: a) the proprieties of starting leady-oxide (composition, morphology, particles size, etc); b) the quantities of water and sulfuric acid added in the mixing stage; c) the temperature, duration and method of mixing; d) the temperature, humidity and duration of curing; e) the stand time of the paste before pasting on the grid [3,14-16].

This paper describes the work that has been carried out in order to investigate more fully the effect of three different methods of curing on the physicochemical behavior of positive plates before, and after, formation in sulfuric acid solution.

We aim to find the conditions under which 3BS are formed and to detect the correlation between the phase composition of plates in the cured and formed states.

EXPERIMENTAL

Paste and Plates Preparation

Positive paste was prepared in a laboratory mixer system, by mixing leady-oxide powder namely Balox (Barton pot variety) with a definite quantity of water, and 8%(wt.) with respect to the leady-oxide, sulfuric acid (1.4 g/cm^3) [17]. The prepared paste was applied to grid cast from Pb-Sb alloy (4% Sb). The resulting positive plates were cured according to the following three methods:

A. In an industrial curing micropilot provided with temperature and humidity controls and air recirculation system, in two steps a) at 36^{0}C and 75% relative humidity (RH) for 16h and b) at 40^{0}C and 40% RH for 48h.

B. Air-dried at 20^{0}C in a closed curing chamber for 36h, without any control of humidity. The moisture content of the plates provided the humidity themselves.

C. Air-dried at 20^{0}C, closed in a polyethylene sheet for 72h.

After curing all plates were dried at 70^{0}C until the moisture content not exceed 2.0 %(wt).

Samples of leady-oxide, uncured and cured pastes were analyzed by X-ray diffraction (XRD) phase-analysis method, scanning electron microscopy (SEM) and wet chemical analysis. The XRD patterns were recorded with a C. Zeiss Jena URB-1988 diffractometer using CuK_α radiation and with an APX-60 complex program the phase composition was determined. SEM studies using a TESLA BS-340-1999 scanning electron microscope were carried out for crystal morphology and structure analysis. By wet analysis, the lead, lead oxide (free and bond in basic sulfates) and lead sulfates (free and bond) were determined.

Plates Formation

A series of test cells with 1 positive and 2 negative (produced under factory conditions) dried plates were assembled. After a soaking for 72h in H_2SO_4 (sp.g. 1.05 g/cm^3) the plates were formed in 0.8M H_2SO_4 solution according to the following protocol: 2h-1A/cell; 1h break; 10h-1.85A/cell; 1h break; 4h-1.50A/cell; 3h-0.85A/cell. Samples of these formed plates, after washing in running water and drying at 125^{0}C for 10h were subjected to phase compositions, morphology and chemical composition analysis.

Battery Performance

Electrical performance tests (nominal capacity, cold cranking ability, charge acceptance and reserve-capacity) were carried out on a series of 12V/45A batteries manufactured using the three cured types of plates.

RESULTS AND DISCUSSION

The changes in phase composition and crystal structure of materials were observed as a function of curing method. Samples of leady oxide uncured and cured paste and formed plates were subjected to X-ray diffraction and wet chemical analysis. The morphology of the materials was examinate by scanning electron microscopy.

1. Leady-oxide

The phase composition and the physico-chemical characteristics of leady-oxide precursor are presented in Table 1.

The crystal structure, obtained by SEM, shows that the oxide phase consists mainly of individual "particles" of varying shape and diameters in the range 2-10 μm (Fig.1a).

Table 1.

Phase composition and physico-chemical characteristic of leady-oxide.

Pb (wt.%)	α-PbO (wt.%)	β-PbO (wt.%)	Acid adsorption (mg H_2SO_4/g)	Water adsorption (ml H_2O/Kg)	Density (g/cm^3)
24	71.40	4.60	185	139	3.50

SEM micrography obtained at higher magnification show that the "particles" are in fact aggregates of various tiny grain which contains numerous small pores (Fig.1b). These pores serve to increase the surface area and explain the high reactivity of leady-oxide (Table 1).

From the above results (Fig. 1. and Table 1.) we have seen that the leady-oxide used as precursor in this work is of good quality [5,7,9].

2. Uncured Paste

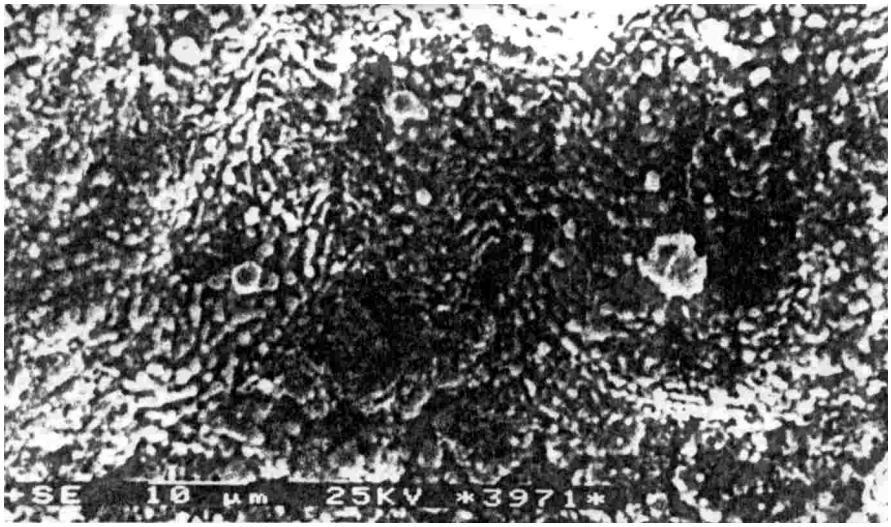
The mixing times (30 min.) and temperature (55 - 60^{0}C) were selected so that the only basic lead sulfate formed was 3BS [5].

Chemical analysis data of the prepared paste show that during the mixing, the level of free lead remains largely unchanged but a significant part of PbO converts to lead sulfates (Table 2).

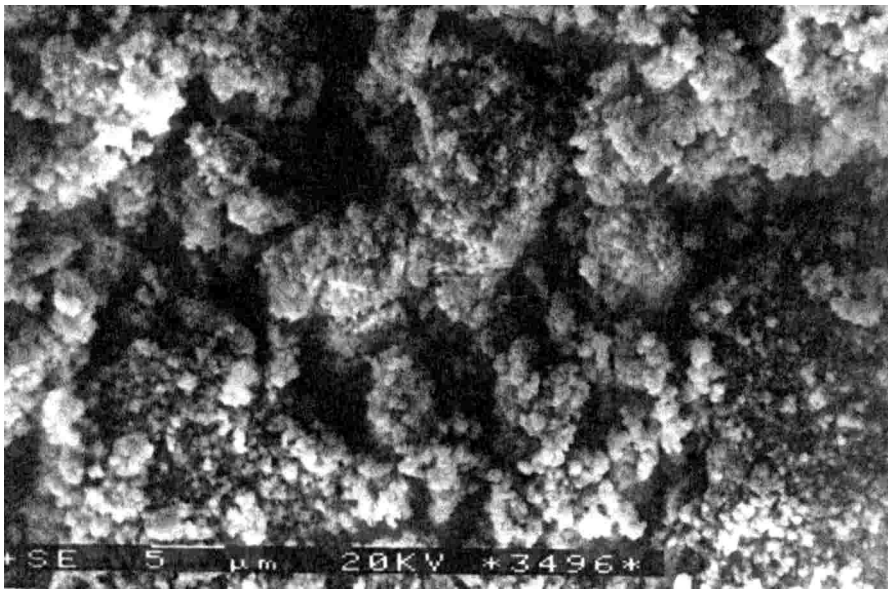
Table 2.

Composition (wt.%) of the prepared positive paste.

Pb	PbO	$PbSO_4$	H_2O	Density (g/cm^3)
22.50	44.22	22.70	10.58	3.78



a)



b)

Fig.1. Scanning electron micrographs of leady-oxide. Magnification bar: a)10 µm and b) 5µm.

The SEM investigations show clearly that the phase morphology of the paste changes from the spherical shape of the precursor oxide to the needle-like form of three basic lead sulfate crystals (Fig. 2).

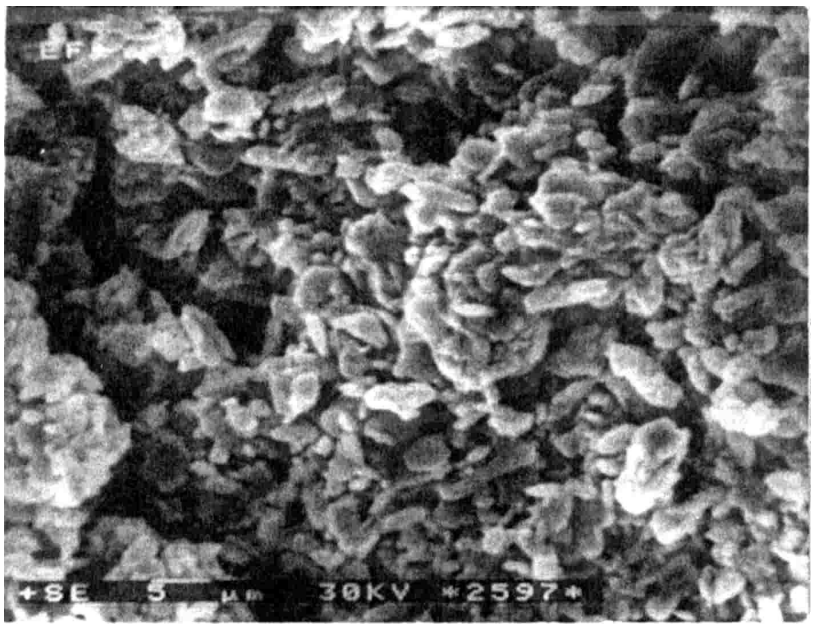


Fig. 2. Scanning electron micrograph of uncured paste.

Because the prepared positive plates were set aside under ambient conditions (up to 8h) until the production run was completed, an investigation was made to determine whether this residence time before curing exerted an influence on the paste composition. Accordingly, phase analysis were conducted every 2h. For all analyzed samples the average $PbSO_4$ content was about 23 wt.%. This fact shows that the paste had already reached a stable composition during mixing and remained virtually unchanged throughout the stand period before curing.

3. Cured Plates

The results of phase composition analysis performed by X-ray diffraction on cured materials are given in Table 3.

Table 3.

Phase-analysis for different cured positive plates.

Curing method	α-PbO (wt.%)	3BS (wt.%)	1BS (wt.%)	HC (wt.%)	Pb (wt.%)
Method A	56.00	36.20	-	7.80	-
Method B	64.05	26.67	-	3.65	5.63
Method C	56.54	30.84	2.87	6.29	3.46

It can be seen that at the end of curing the lead content in paste decreased considerably in all three curing methods due to their conversion to α-PbO. No 4BS were formed. Very little amount of 1BS (variety, which is harmful to battery performance,) was formed in the plates cured under polyethylene sheet.

Basic lead carbonate (HC) is formed in all the curing methods. The formation of carbonate roughens the surface of 3BS crystal [13]. This improves the contact between the crystals and, consequently the toughness of the paste.

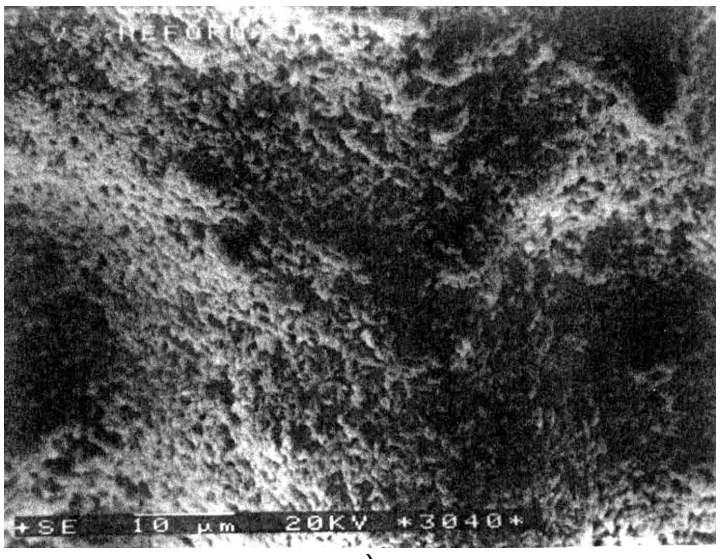
The amount of 3BS, the predominant species of basic lead sulfate in active cured materials depends on curing method. It is clearly that during curing in a highly humid atmosphere, method A, the remaining metallic lead from the precursor paste is oxidized, while the 3BS phase content increases.

The level of 3BS in plates materials cured under polyethylene sheet is higher than those cured by method B (in closed chamber) but the first contains 1BS and cracking and partial shedding of pastes were observed.

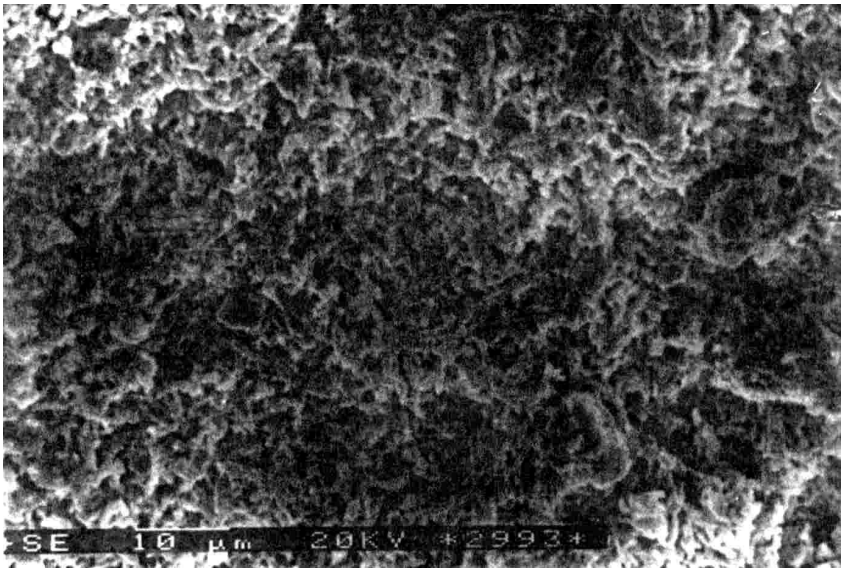
The higher free lead content of plates cured after method B and C provides evidence that the curing process was incomplete (has been stalled probably, by the lower humidity level existent in the chamber).

The above observations confirm that the cured material phase-composition is largely dependent on the humidity level and its variation during the process.

From the SEM micrographs of different cured plates it is seen that the curing has affected the material crystal structure (Fig. 3. a, b and c). In general the small sized crystals of various shapes interconnected in a homogenous structure are attributed to 3BS and to unreacted α-PbO.



a)



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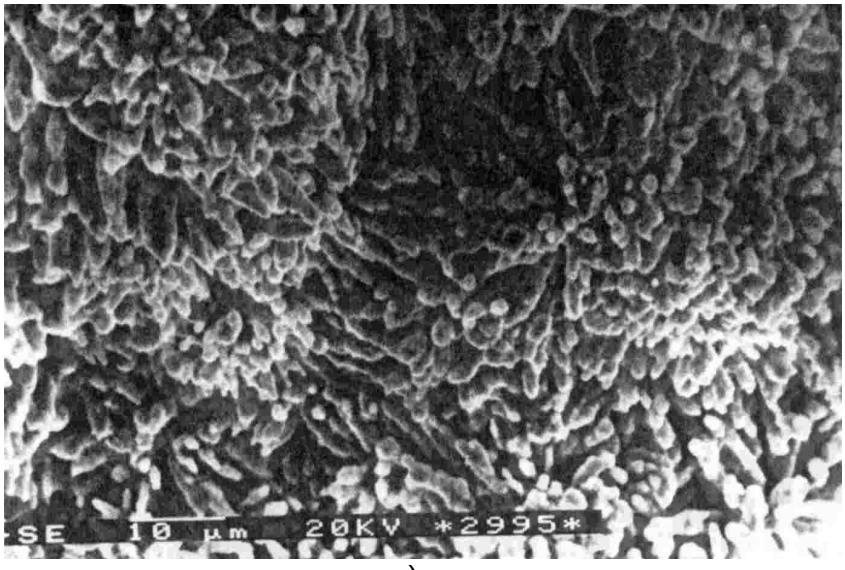

c)

Fig. 3. Scanning electron micrographs of different cured plates:
a) micropilot; b) closed chamber and c) polyethylene covered.

Pavlov [2] and Zerroual [7] reported similar micrographs on synthesized 3BS from PbO and H_2SO_4.

The 3BS formed during curing (A method) consists of needles with relative equal size (1.5-2.0 μm), while the 3BS crystals formed in the plates cured after C method are slightly larger (3-7 μm) without definite shape (Fig. 3 a and b).

From the electron micrographs given in Fig. 2 and Fig. 3 (b and c) we can say that the 3BS cured material crystals is slightly larger that those in the precursor paste. This indicated that at low temperature (20^0C) a recrystallization of 3BS has occurred during curing process but no recrystallization has occurred at higher temperature (method A).

4. Formed Plates and Battery Tests

During formation two main reactions can be distinguished. First, due to the soaking of plates in the electrolyte, the basic lead sulfates are partially converted into lead sulfate. Simultaneously, the lead and/or the lead basic sulfate are electrochemically oxidized leading to charge active material PbO_2. Table 4 gives the XRD analysis of the formed active materials.

Table 4.

X-ray diffraction analysis of formed active mass (wt.%).

Curing method	PbO	$PbSO_4$	Pb	PbO_2	α-PbO_2	β- PbO_2
Method A	9.33	1.68	-	88.99	7.83	81.16
Method B	12.43	5.35	2.76	79.46	12.18	67.28
Method C	12.38	3.56	0.73	83.33	10.09	73.24

The results shows that the active mass of plates previously cured after method A lead to a higher PbO_2 content than those cured under conditions B and C. In addition, the formed active material cured in micropilot contains after oxidation more β-PbO_2 and the formed plates derived from material cured after method B and C still contains appreciable levels of unoxidized residues, i.e. PbO, $PbSO_4$ and Pb. It can be concluded therefore that the conditions of curing have a notable effect on the level of PbO_2 active mass formation. From the above results we can seen that the larger the amount of 3BS paste content, the larger will be the β-PbO_2 amount in the formed active mass (Table 3 and 4).

After formation, the fully charged state of the cell was achieved by applying a constant current (2.25 A) until both the terminal voltage and the acid density (1.28 g/cm^3) were kept constant for two hours.

For the determining of nominal capacity, C_{20}, the full charged batteries were discharged at a constant current of 2,25 A until the terminal voltage fell to 10.5 V. The product between the current intensity and the discharge time yields the nominal capacity.

For the determining of charge acceptance, the fully charged batteries were discharged with a constant current I = $0.1C_{20}$ A, at 25^0C. The batteries were then kept at 0^0C for 25 hours and fully charged at a 14.4 V constant voltage. The current intensity value after 10 min. charge was recorded.

In the reserve-capacity tests, the fully charged batteries were subjected to two complete C_{20} charge-discharge cycles and deposited for 28 days at (20 $\pm$ 5)^{0}C. The batteries were then discharged at 0.05 C_{20} A, until the terminal voltage was 10.5 V. The measured reserve capacity was reported to the initial capacity. In the cold-cranking ability tests, after three complete C_{20} charge-discharge cycles, the fully charged batteries were kept at -18^0C for 24h. The batteries were then discharged at 3.5 C_{20} A and the recorded time until the terminal voltage to fell to 6 V was taken as a measure of cold-cranking ability.

Table 4 summarizes the electrical testing results of batteries manufactured using the three different cured plates. The results were recorded after technical requirements for quality included in Romanian STAS 444/1 - 74.

Table 5.

Electrical batteries parameters.

Electrical characteristics	Method of curing (A)	(B)	(C)
Initial capacity, $E_{xp.}/C_{20}$ (%)	109.8	100	104
Charge acceptance (A)	6.85	6.15	7.55
Reserve capacity (%)	93	83	85
Cold-cranking ability (sec.)	185	182	184

In the light of these results, it can be seen that the positive plate active mass previously cured by method A gives the highest electrical performance.

This could be attributed to the large β-PbO_2 and total PbO_2 contents since the capacity of β-PbO_2 (0.164 Ah/g) is larger than that of α- PbO_2 (0.135 Ah/g) [18]. Because during lead-battery discharge, the potential of negative plate is the first to reach the cut-off value, the cold-cranking ability (deep discharge at - 18^0C) of battery is "negative-potential limited" [4]. Thus this propriety is not so much affected by positive plate structure.

The obtained results give us ground to conclude that curing methods B and C are not a successful technology for positive plates production.

CONCLUSIONS

The above investigation illustrates that curing conditions are determinant for the modifications of the chemical and phase composition of positive active mass and for the electrochemical performance. Thus, a better understanding of the curing mechanisms is required in order to optimize the positive plate's performance.

It has been observed that the key to successful curing is the maintenance of an exact balance between the moisture contient, temperature and duration of process (method A). It is essential to conduct the curing in an enclosed chamber that allows precis regulation of the ambient conditions.

Further experimental work is required to determine in detail, the influence of these parameters on curing reactions.

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