ADSORPTION OF AN ORGANIC EXTENDER ON LEAD SULFATE CRYSTALS

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In the discharge of the negative electrode of a lead accumulator, a supersaturated solution, from which lead sulfate crystallizes, is formed at the electrode/solution interface. The surface of the negative electrode is covered by a layer of lead sulfate crystals, which restricts the duration of the discharge of the electrode, particularly at high discharge current densities [1]. It is known that the organic materials used as extenders in the active mass retard the onset of the anodic passivation of the lead electrode and that the action of these substances involves an adsorption mechanism [1, 2]. There is as yet lack of agreement regarding the details of the mechanism of the adsorptive action of extenders in the anodic polarization of the negative electrode. For example, the increase in the dimensions of the crystals of electrodeposited lead sulfate in the presence of extenders [3, 4] has been attributed [4] to the restriction of the process of formation of lead sulfate crystallization centers on the surface of a lead electrode covered with adsorbed molecules of the extender.

It was previously shown [2] that an effective extender is adsorbed on lead. This was confirmed by measurements of the capacity of the electrical double layer [2] and the hydrogen overpotential on spongy lead [2, 5]. It was also shown that organic substances may also be adsorbed on the surface of $PbSO_4$ crystals [1, 6]. In [1-3], however, the authors assumed that the increase in the technological capacity is due to the adsorption of the organic extender not on lead but on lead sulfate [1]. This agrees with the results of a study of the structure of an electrolytic deposit of lead sulfate by means of the electron microscope: the lead sulfate formed on anodic polarization of the electrode in the presence of an organic extender has a coarsely crystalline structure [3].

The present paper describes a continuation of the study of the influence of an organic extender on the study of the influence of an organic extender on the structure of chemically precipitated lead sulfate. The precipitation was carried out from 9.6 N sulfuric acid solution with and without an organic extender (tanning agent No. 4), by the gradual addition of a saturated solution of $Pb(NO_3)_2$ at room temperature. This method ensures an excess of HSO_4^- ions during the crystallization of lead sulfate, as is the case during the discharge of an accumulator. The lead sulfate precipitates were washed repeatedly with water and dried with acetone. The photomicrographs, obtained in an electron microscope, of carbon replicas from the lead sulfate crystals are shown in Fig. 1, a and b. It can be seen from the photographs that the crystals of lead sulfate precipitated in the absence of the extender have dimensions of 0.3-0.8 μ, which is several times smaller than the resolving power of the light microscope used in the analogous studies in [4]. The sulfate crystals precipitated in the presence of the extender have the same shape but much larger dimensions (1-3 μ).

Thus the study of the morphology of lead sulfate crystals by means of the electron microscope has shown that an organic extender also influences the structure of the sulfate obtained by chemical precipitation from a solution of a lead salt in acid medium, under conditions in which the influence of the lead support on the crystallization is eliminated. These results confirm the previously proposed [1, 5] mech-

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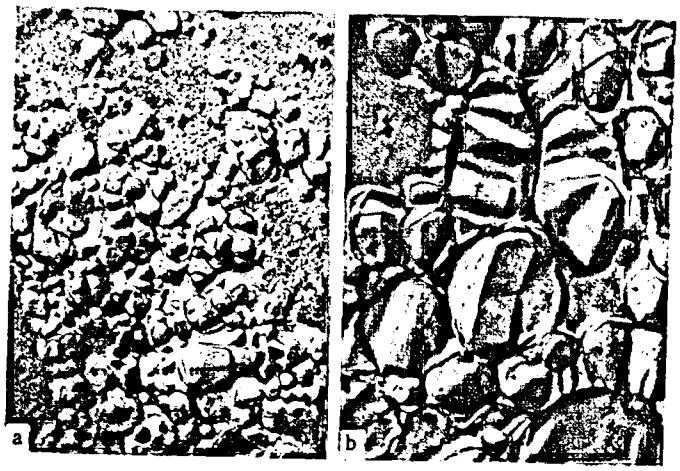

Fig. 1. Electron microscope photographs of carbon replicas from $PbSO_4$ crystals obtained by precipitation from saturated $Pb(NO_3)_2$ solution without (a) and with (b) the addition of an organic extender (magnification 6000).

anism of the influence of an extender on the structure of lead sulfate obtained in the anodic polarization of lead in sulfuric acid solution.

This view is also in agreement with the results of work on the study of the influence of added $BaSO_4$ on the mechanism of action of extenders [7].

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