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INFLUENCE OF ADDITIVES ON POLARIZATION CAUSED BY CHANGES
OF THE RATE OF CRYSTALLIZATION AND DISSOLUTION OF PbSO_4
ON THE NEGATIVE ELECTRODE OF THE LEAD STORAGE CELL

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Various surface-active substances, known as expanders, are introduced into the active material of the negative electrode to improve the electrical characteristics of the lead battery, especially in starter operation.

It was shown earlier [1, 2] that during discharge of the negative electrode polarization occurs as the result of supersaturation of the solution in the layer adjacent to the electrode with lead sulfate, not only at the start, when there is a deficiency of crystal nuclei (the so-called "whiplash"), but throughout the discharge. The supersaturation is due to retarded growth of PbSO_4 crystals. This supersaturation increases in presence of surface-active substances which are adsorbed on PbSO_4 crystals and retard their growth. It was also shown that retardation of dissolution of PbSO_4 crystals in presence of certain organic substances which are adsorbed on them limits increase of the cathodic charging current of the negative electrode [1, 3]. These conclusions are consistent with the observation of Kolthoff et al. [4] that organic surface-active substances may retard dissolution and crystallization of many salts.

We have investigated the influence of expanders, both recently proposed and in established use in the battery industry, on the rate of dissolution of lead sulfate during cathodic polarization (charging) of a discharged negative pasted lead electrode, and on ionization of lead at the start of anodic polarization of a well-charged electrode. The experiments were conducted on electrodes $47 \times 47 \times 2.3$ mm in size, in excess electrolyte. The cell assembly consisted of one negative test electrode and two auxiliary positive electrodes. The potential of the negative electrode was measured against a mercury-mercurous sulfate reference electrode with acid of the same concentration as in the test cell, i.e., 9.6 N.

The influence of various additives on the limiting rate of the main cathodic process was studied by recording curves for the dependence of the cathodic current density on the potential at electrodes previously discharged to 50% of their actual capacity. It was shown earlier [3] that it is possible to estimate the maximum rate of lead sulfate dissolution, which controls the rate of the overall process at high current densities, from the limiting current of lead sulfate reduction under certain conditions. In order to eliminate the influence of additives on the hydrogen overpotential, which alters the values of the limiting charge current, instead of the limiting current we used the charge current at an overpotential $\Delta\phi = 0.1$ V of lead sulfate reduction, which is proportional to the limiting current.

The curves for the dependence of the electrode potential on the current density (A/cm^2 of apparent surface area) are shown in Fig. 1 (upper curves), while the current densities at a cathodic overpotential $\Delta\phi = 0.1$ V for electrodes with all the additives studied and in absence of additives are given in Table 1.

Apart from electrodes without expanders (Table 1, compositions Nos. 1, 2, 4, 5), the highest current densities at $\Delta\phi = 0.1$ V are obtained for electrodes containing BNF* in the active material together with BaSO_4 , if

*BNF is the product of condensation of crystalline phenol and β -naphtholsulfonic acid with formaldehyde [5].

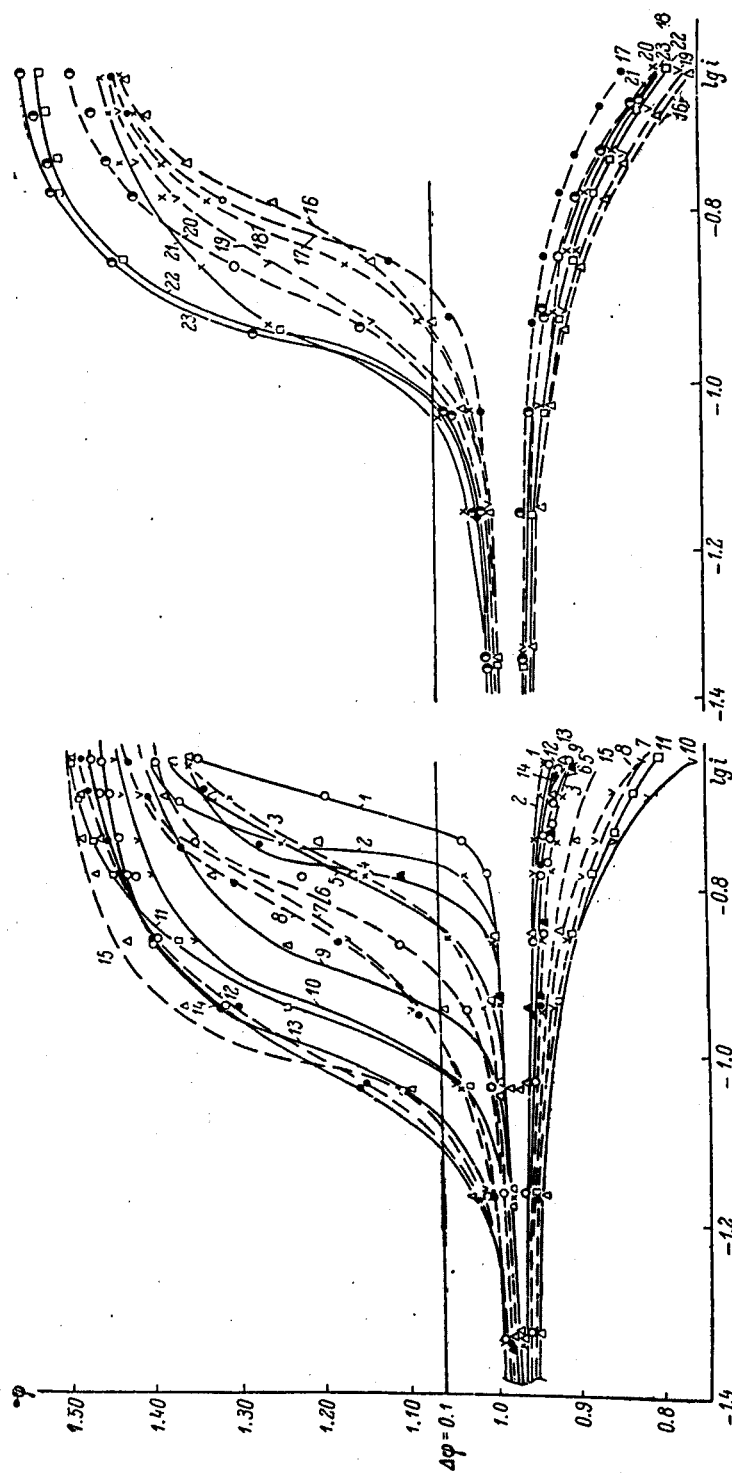


Fig. 1. Influence of additives on the current density during cathodic (upper curves) and anodic (lower curves) polarization of negative electrodes. ϕ) Electrode potential (V); $\log i$) logarithm of the current density (A/cm^2); the same in Figs. 2 and 3. 1-23) Numbers of curves and of the compositions in Table 1.

TABLE 1

Com- posi- tion No.	Additives in active material of negative electrode	Cur. density $i \cdot 10^2$ (A/cm ²) at cath. overpot. 0.1 V	Initial anodic over- potential of lead (mV) at $i = 0.025$ A/cm ²
1	No additives	18.6	30
2	BaSO ₄	17.0	21
3	BNF + MgSO ₄ + BaSO ₄	14.3	33
4	Akuvit + BaSO ₄	15.7	21
5	Akuvit	14.5	38
6	BNF + Al ₂ (SO ₄) ₃ + BaSO ₄	12.6	31
7	BNF + CdSO ₄ + MgSO ₄ + Al ₂ (SO ₄) ₃ + BaSO ₄	10.6	39
8	BNF + CdSO ₄ + BaSO ₄	10.6	24
9	DSV + BaSO ₄	11.3	22
10	Humic acid + BaSO ₄	10.3	31
11	Induline + BaSO ₄	9.5	34
12	BNF + Akuvit	8.0	41
13	BNF + BaSO ₄	8.5	37
14	BNF + Akuvit + BaSO ₄	7.9	23
15	BNF + C ₆ H ₆ O ₆ + BaSO ₄	8.3	36
16	Humic acid + CdSO ₄ + BaSO ₄	11.6	33
17	Humic acid + MgSO ₄ + BaSO ₄	12.7	31
18	Humic acid + CdSO ₄ + MgSO ₄ + Al ₂ (SO ₄) ₃ + + BaSO ₄	11.3	26
19	Humic acid + BaSO ₄	10.3	31
20	Humic acid + Al ₂ (SO ₄) ₃ + BaSO ₄	10.1	30
21	Induline + CdSO ₄ + MgSO ₄ + Al ₂ (SO ₄) ₃ + BaSO ₄	9.1	28
22	Induline + BaSO ₄	9.5	34
23	Induline + Al ₂ (SO ₄) ₃ + BaSO ₄	9.5	31

MgSO₄ or Al₂(SO₄)₃ is added to them. The sulfates of Cd, Mg, and Al improve somewhat the performance of electrodes containing humic acid as an expander, but have virtually no influence on electrodes containing induline.* In absence of these additives, BNF gives the lowest current density at $\Delta\varphi = 0.1$ V of all the organic expanders studied, and DSV† the highest. The minimum current density at $\Delta\varphi = 0.1$ V is obtained on addition of Akuvit‡ to the active material of electrodes containing BNF together with BaSO₄.

Thus, in absence of added salts (apart from BaSO₄) the expander DSV gives the highest charge-current density of the organic expanders tested. The most effective of the additives increasing the charge current are MgSO₄ and Al₂(SO₄)₃.

At equal polarization (e.g., 0.1 V) a correlation exists between the cathodic and anodic currents (Fig. 1), although there are deviations from the series. The explanation of the correlation is that both during charge and during discharge of half-discharged negative electrodes the polarization is essentially of the same (concentration) type, due to the low rate of dissolution and growth of PbSO₄ crystals. Slow dissolution causes greater relative changes in the concentration of the salt solution than does slow crystallization, and this leads to greater retardation under the influence of cathodic current.

The influence of various additives on the initial fall of potential during discharge of the lead electrode, known in industry as "whiplash," was studied with the aid of φ vs log i curves. These experiments were also conducted in sulfuric acid of density 1.280 g/cm³ (9.6 N) as the electrolyte. Before the curves were recorded the negative electrode was fully charged at $9 \cdot 10^{-3}$ A/cm² current density until the potential remained constant during the last 3 h of charge. It was assumed that this resulted in complete reduction of all the lead sulfate crystals which might otherwise act as crystallization nuclei for deposition of PbSO₄ during subsequent anodic polarization, or that the residual crystals are poisoned to the extent that they cannot dissolve at concentrations below saturation or grow in a supersaturated solution (so-called "irreversible sulfation").

The anodic current was measured with an ammeter of M104 type, class 0.5; a bridge circuit with an R-307 potentiometer was used for measurement of potential. Some of the results are shown in Figs. 2 and 3. Measurements of the equilibrium potentials (correct to 0.001 V) of all the electrodes studied gave a value of approximately 0.966 V.

Comparison of the values obtained for the anodic overpotential of lead on fully charged (Table 1) and 50% discharged (Fig. 1, lower curves) negative electrodes at $i = 0.025$ A/cm² shows no correlation between them with

*Induline is a dye derived from ammonium bases, made in Italy and used in Hungary as an expander.

†DSV is a desulfonated macromolecular fraction of resins from vanillin production [6].

‡Akuvit is an additive devised and used in Hungary for improving battery charging, having the composition CdSO₄ · ⁸/₃H₂O 10%, MgSO₄ · 7H₂O 13%, Al₂(SO₄)₃ · 18H₂O 45%, and tartaric acid 32% [7].

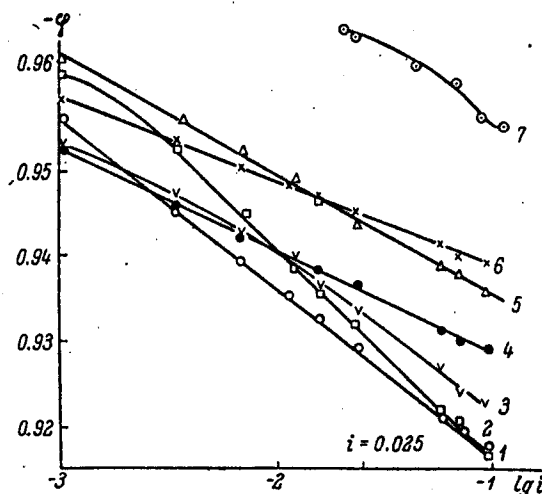


Fig. 2. Influence of additives on the anodic overpotential of lead. On a fully charged electrode: 1) $\text{BaSO}_4 + \text{BNF}$; 2) $\text{BaSO}_4 + \text{induline}$; 3) $\text{BaSO}_4 + \text{humic acid}$; 4) without additives; 5) $\text{BaSO}_4 + \text{DSV}$; 6) BaSO_4 ; on a half-discharged electrode: 7) $\text{BaSO}_4 + \text{BNF}$.

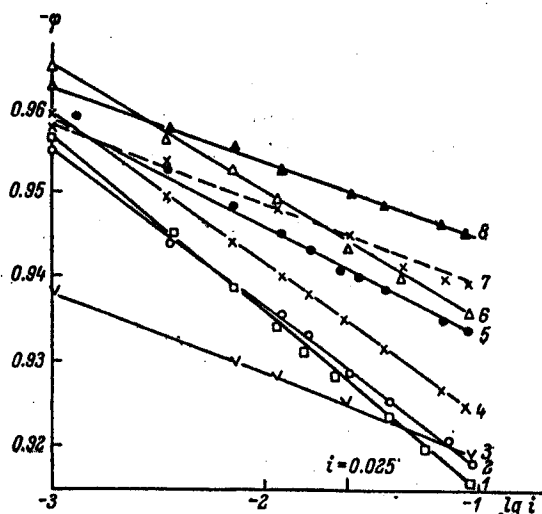


Fig. 3. Influence of additives on the anodic overpotential on a fully charged lead electrode. 1) Akuvit; 2) $\text{BaSO}_4 + \text{BNF}$; 3) $\text{BNF} + \text{Akuvit}$; 4) $\text{BaSO}_4 + \text{BNF} + \text{MgSO}_4$; 5) $\text{BaSO}_4 + \text{BNF} + \text{CdSO}_4$; 6) $\text{BaSO}_4 + \text{Akuvit}$; 7) BaSO_4 ; 8) $\text{BaSO}_4 + \text{BNF} + \text{Akuvit}$.

respect to dependence on the nature of the additive, and indicates that the anodic overpotential on the fully charged electrode, which contains no crystallization nuclei (a small amount of BaSO_4 crystals cannot facilitate crystallization of PbSO_4 sufficiently), is tens of times greater than on the half-discharged electrode. For example, in the case of an electrode containing only BaSO_4 the overpotential in the former case is greater by a factor of 20, and for an electrode containing BNF together with BaSO_4 (Fig. 2) it is greater by a factor of 36.

The determining step of the anodic process on a fully charged negative electrode (at least up to appearance of a PbSO_4 precipitate with a highly developed surface) is diffusion and formation of lead sulfate crystallization nuclei within the diffusion layer rather than electrochemical conversion of Pb into Pb^{2+} , whose overpotential is very low [8], amounting under our conditions at a current density of 10^{-1} A/cm^2 to 1 mV, which is smaller by a factor of 10 than concentration polarization.

The slope of the plots (Figs. 2 and 3) is 0.02–0.01 V, i.e., the process rate depends strongly on the potential. Values of the anodic concentration overpotential of lead under these conditions at 0.025 A/cm^2 current density are given in Table 1. These data show that electrodes containing the expanders BNF and induline together with BaSO_4 in the active material have the highest overpotentials. Initial crystallization of PbSO_4 pro-

ceeds most easily in presence of BaSO_4 (which is isomorphous with PbSO_4). Of course, barium sulfate could completely eliminate the retardation associated with the start of crystallization of PbSO_4 if, present (in a finely divided state) in a sufficient amount on the surface of the active material, it was freed from organic substances adsorbed on its surface; this was evidently not achieved under our conditions. In particular, the total surface area of the BaSO_4 crystals present on the lead surface is very small in comparison with the surface area of PbSO_4 crystals on a partially discharged, e.g., a half-discharged, electrode. Addition of DSV (Fig. 2, curve 5) has virtually no influence. On the one hand, additions of Akuvit or CdSO_4 eliminate the retardation of lead sulfate crystallization caused by BNF in presence of BaSO_4 (Fig. 3, curves 8, 5, and 2). On the other hand, at low current densities BNF increases the retardation caused by Akuvit in absence of BaSO_4 . The other additives retard initial crystallization of PbSO_4 to various extents. The greatest retardation of the start of lead sulfate crystallization at high current densities is produced by induline and BNF, both in presence of BaSO_4 , and also by Akuvit.

The influence of the additives used in the present investigation on the capacity of batteries under conditions of starter discharge was studied earlier [9]. It was shown that batteries whose negative electrodes contain DSV and BNF as expanders together with BaSO_4 in the active material have the highest capacity. The lowest capacity is obtained with the use of induline and humic acid with BaSO_4 .

Our investigation showed that, of all the additives studied, the expander DSV with BaSO_4 gives the highest capacity of batteries operated under starter conditions, ensures the highest limiting charge current, and only slightly retards the start of lead sulfate crystallization during the initial period of discharge of the negative electrode (the so-called "whiplash"). The expander BNF with BaSO_4 , while insuring fairly high capacity of batteries operated under started conditions, lowers the charge current sharply at a cathodic overpotential of 0.1 V, and strongly retards the start of lead sulfate crystallization.

CONCLUSIONS

1. Study of the influence of additives on the charge current of half-discharged negative electrodes at a cathodic overpotential of 0.1 V showed that all four organic expanders tested lower the charge current to different extents owing to retardation of lead sulfate dissolution. The greatest lowering of the charge current is produced by DSV and the smallest by BNF. Electrodes with additions of humic acid and induline have somewhat smaller charge currents than electrodes with DSV. Addition of Akuvit to the active material of an electrode containing BNF does not raise the charge current, whereas additions of MgSO_4 or (to a smaller extent) of $\text{Al}_2(\text{SO}_4)_3$ and CdSO_4 do.

2. Study of the anodic overpotential of lead on fully charged negative electrodes confirmed the opinion advanced earlier that the controlling step of the anodic process at the start of discharge is formation of nuclei of lead sulfate crystals and not the electrochemical process $\text{Pb} \rightarrow \text{Pb}^{2+}$. The expander DSV with BaSO_4 only slightly retards the start of crystallization of PbSO_4 . Induline and BNF have the strongest retarding effect on crystallization in presence of BaSO_4 . Akuvit, CdSO_4 , and MgSO_4 partially counteract the retardation caused by BNF in presence of BaSO_4 .

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