

changes of pH in the diffusion layer have a substantial influence on the kinetics of hydrogen evolution on aluminum but do not provide a complete explanation of the nature of the negative difference effect.

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MECHANISM OF THE INFLUENCE OF EXPANDERS ON THE ACTION OF THE NEGATIVE ELECTRODE OF THE LEAD STORAGE CELL

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Despite the great variety of various chemical sources of current which have appeared since the invention of the lead storage cell, during the next one or two decades the lead cell, with certain improvements, will remain unrivaled [1, 2]. During the 115 years of its existence the lead cell has undergone considerable changes. The specific characteristics have been improved, the life has been lengthened, and self-discharge and sulfation (irreversible passivation of the electrodes of lead batteries) have been diminished. Further improvement of lead-acid batteries is an important technical problem.

Since as long ago as 1881, from the time of invention of pasted plates by Faure and Brush, a significant role in work on improvement of the characteristics of lead batteries has been assigned to searches for various additives introduced into the active material of the negative (and sometimes also of the positive) plate. In a review published in 1947, Ritchie [3] lists some 400 substances which have been found quite empirically and patented as additives introduced either into the active material or into the electrolyte. Despite the strenuous efforts made in various countries to find the most effective additives, up to now the coefficient of utilization of the active material does not exceed 60% even under the most favorable operating conditions. Empirical selection of expanders* from the wide variety of known organic and inorganic compounds is extremely laborious and ineffective. Accordingly, development of the theory of expander action is of undoubted interest. The problem of the mechanism of expander action is intimately linked with the problem of the mechanism of adsorption of organic substances on electrodes, developed mainly by Frumkin [4, 5] as long ago as 1925 and extended in later work by Frumkin and his school [6, 7]. Interest in studies of adsorption of organic substances on solid electrodes has grown in recent years, but we will not discuss them in detail here, as they are dealt with fully in monographs and papers on the subject [8-11], and will consider only investigations relating to the lead electrode.

*Expanders are substances introduced into the paste of negative plates to increase their discharge capacity.

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Kabanov et al. estimated the potential of zero charge on lead in sulfuric acid [12] and investigated the influence of various organic substances on the hydrogen overpotential in this system [13], on the overpotential of lead discharge and ionization, and on the thickness of the passivating lead sulfate film on the electrode [14]. It was postulated that two mechanisms of anodic formation of lead sulfate are possible in principle: 1) by its direct formation (in the solid phase) on the electrode, and 2) as the result of accumulation of the products of lead dissolution in the layer adjacent to the electrode during anodic polarization, followed by their diffusion and precipitation on the electrode. The second mechanism can explain with fewer assumptions the growth of the lead sulfate layer from the electrode into the solution. It was shown earlier [14] that valeric acid, phenol, sucrose, and amyl alcohol are adsorbed on lead, as is shown by their influence on the hydrogen overpotential and on the capacity of the electric double layer, and yet these substances do not affect the thickness of the passivating layer. However, although the dye Methylene Blue does not alter the hydrogen overpotential on lead it increases the thickness of the passivating layer, i.e., it acts as an expander; this was attributed to adsorption of this dye on the lead sulfate crystals, modifying their habit, with a resultant decrease of the passivating action of the layer of these crystals. As was shown earlier [14], this mechanism of action of surface-active substances is in good agreement with the data of Kolthoff and Rosenblum [15] on the influence of certain dyes on the rate of dissolution of crystals and crystallization of salts, and with the observations of Davis and France [16] on the influence of Methylene Blue on the habit of lead nitrate crystals.

According to Lorenz [18] the influence of expanders on the discharge capacity of the negative electrode is attributable to adsorption of surface-active substances on lead and not on crystals of lead sulfate. By this concept surface-active substances adsorbed on the electrode inhibit formation of lead sulfate crystal nuclei, and this favors growth of individual crystals. Lorenz considers that adsorption of an expander on lead sulfate accelerates electrode passivation, because growth of lead sulfate crystals is hindered and passivation proceeds by formation of new crystallization centers; however, this hypothesis contradicts experimental data [17] on the influence of surface-active substances on the habit of lead sulfate crystals formed by chemical precipitation. The influence of an added expander on the structure of chemically precipitated lead sulfate was investigated earlier [17]. The precipitation was conducted by gradual addition of saturated $\text{Pb}(\text{NO}_3)_2$ solution at room temperature to 9.6 N sulfuric acid solution containing an organic expander (tanning agent No. 4), and to the same solution without additives. This procedure ensures an excess of HSO_4^- ions during crystallization of lead sulfate, which is the case during discharge of the lead cell. Electron-microscope study of the morphology of lead sulfate crystals showed that the organic expander increases the size of lead sulfate crystals obtained by chemical precipitation from a solution of a lead salt, i.e., under conditions excluding the influence of the support on crystallization. These results confirmed the mechanism postulated earlier [14] for the influence of the expander on the structure of the lead sulfate deposit obtained during anodic polarization of lead in sulfuric acid.

During operation of a lead battery the active material of the negative electrode undergoes repeated changes of lead into lead sulfate and vice versa. For prolonged operation of battery plates the structure of the charged plate must remain unchanged in the course of cycling; otherwise swelling or sintering of the active material may occur. The surface-active substances introduced into the active material are generally adsorbed both on the lead sulfate crystals and on lead, affecting the habit of the crystals formed during discharge or charge, and thus influence the structure of the active material in the negative plate. The influence of expanders on the structure of the active material during forming and operation of negative plates has been investigated by optical methods by Simon, Caulder, Gurlusky, Pierson, and Sharpe [19-22]. Pierson [19] showed that lignin alters the habit of the lead crystals growing during the forming process. The size of the lead dendrites in the formed plate diminishes in presence of lignin. Microscopic investigation of cycled plates in the charged state [20] showed that lignin has the same effect in this case as during the forming process. The lead dendrites were smaller in plates containing lignin than in absence of lignin. It follows from literature data [20] that the lead particles grow in the course of cycling, but lignin retards this process. In a microscopic study of the structure of lead and of lead sulfate formed during cycling of lead batteries, Simon et al. [21] concluded that the favorable influence of lignin on the discharge characteristics of the lead electrode is due not only to its action on the structure of the layer of lead sulfate crystals but also to its influence on the habit of the lead crystals. Sharpe [22] carried out a spectrophotometric study of the adsorption of calcium lignosulfonate on lead powder and on lead sulfate crystals. In Sharpe's opinion the improvement of the electrical characteristics of the lead electrode by introduction of a small amount of calcium lignosulfonate into the paste can be attributed to the dispersing action of the lignosulfonate, preventing gradual growth of the particles of lead powder.

The above literature review shows that surface-active substances influence the habit both of lead sulfate crystals and of the lead crystals formed during discharge. At the same time, it is evident that molecules of surface-active substances adsorbed on the metal must influence both the structure of the electric double layer [23] and the kinetics of discharge and ionization of the metal [24].

The first measurements of the differential capacity of the electric double layer on lead in presence of organic compounds by the ac method were performed by Borisova, Ershler, and Frumkin [25]. They showed that at potentials close to the potential of zero charge introduction of amyl alcohol into the solution leads to a substantial decrease of the differential capacity on lead, as on mercury, indicating that adsorption of amyl alcohol occurs in this region of potentials. At a potential far on the negative side of the potential of zero charge of lead the curve for the dependence of the differential capacity on the potential had a capacity peak corresponding to desorption of amyl alcohol from the electrode surface at that potential. Adsorption of a mixture of naphthol, thymol, and diphenylamine [26], α - and β -naphthol and diphenylamine [27], and hexyl alcohol [28] was studied later.

It was shown in certain investigations [9, 11, 25-28] that the relationships for adsorption of organic molecules on metallic electrodes [4-7], derived mainly by analysis of experimental data for the mercury electrode, describe qualitatively the behavior of organic molecules also on a lead electrode. Comparison of the experimental relationships with theoretically derived expressions made it possible to calculate the numerical values of the adsorption parameters of the above-named organic compounds [29-31]. Measurements of the capacity of the electric double layer in presence of expanders have been reported [32, 33]. Sharpe [32] compared the influence of the phthalein group and of ammonium lignosulfonate on the technological and double-layer capacities of lead. It follows from literature data [32] that the most active of the expanders studied, cerulein, lowers the capacity of the double layer considerably at all potentials studied on the cathodic side of the equilibrium potential of lead in sulfuric acid, and lowers the pseudocapacity which is apparently due to formation of lead sulfate in the region of the equilibrium potential. Rhodamine B lowers the capacity slightly, and only at high cathodic potentials. This substance is the least active expander of all those studied [32]. Brennan and Hampson [33] studied adsorption of various commercial expanders, derivatives of lignosulfonic acid, on lead. Introduction of these expanders into the solution leads to lowering of the capacity of the electric double layer over a wide range of potentials corresponding to a negatively charged lead surface. Curves for the dependence of the double-layer capacity on the potential [33] show that at considerable negative surface charges the expander is desorbed from the electrode surface, but this is not accompanied by the desorption peak characteristic of such cases. The authors cited attribute the absence of a peak to the high molecular weights of the expanders studied.

According to Sharpe [32], measurements of the differential capacity at a smooth lead electrode in presence of organic substances may be used for selection of the most effective expanders for the negative plate of the lead cell. However, it should be pointed out many organic compounds leading to depression of the double-layer capacity on lead are known, but very few of them are effective expanders. Moreover, the region of potentials accessible to measurements of double-layer capacity is considerably more negative than the equilibrium potential of lead, and substances which are adsorbed effectively near the potential of zero charge may be desorbed from the positively charged lead surface at the equilibrium potential. There is no doubt that adsorption of expander molecules on the electrode surface may lead to changes in the rate and possibly in the mechanism of discharge and ionization of lead and may influence the hydrogen overpotential and the probability of formation of nuclei of sulfate crystals on the lead surface during anodic dissolution of lead in sulfuric acid; at the same time, adsorption of these surfactants has a significant influence on the habit of lead sulfate crystals [14, 17]. A paste electrode is a highly complex electrochemical system, and in our opinion measurements of double-layer capacity in presence of expanders, while assisting interpretation of the mechanism of action of these substances on certain processes, cannot serve as criteria of expander activity.

As noted above, two mechanisms of anodic formation of lead sulfate in sulfuric acid have been postulated: by diffusion of the reaction products into the solution volume, followed by precipitation on the electrode, and by a solid-phase process. In discussions of the favorable influence of expanders on the discharge capacity of the lead electrode, Harrison et al. [34-36] put forward the hypothesis, which is not fully substantiated in our view, that expanders have an inhibiting effect on the process occurring in the solid phase. With retardation of the solid-phase process the anodic formation of lead sulfate proceeds, in the opinion of the authors cited, predominantly by the parallel route: through the stage of dissolution and subsequent precipitation of the salt. Brennan and Hampson [33, 37] also hold this view, but in their opinion the above explanation is not exhaustive.

Quantitative investigation of the influence of surface-active substances on the mechanism and kinetics of discharge and ionization of lead in sulfuric acid is hindered by formation of an insoluble precipitate on the lead surface. Conditions such that the lead surface is free from a precipitate during anodic dissolution are the most favorable for analysis of the results. The influence of 1,5-dihydroxynaphthalene and of two expanders used in storage batteries, BNF and tanning agent No. 4, on the structure of the electric double layer and on the impedance of the lead electrode, has been investigated [38-41]. The impedance components were measured at the

equilibrium potential in acidified potassium nitrate solutions with additions of lead nitrate and surface-active organic substances. It was shown [41] that in absence of additives the reaction of discharge and ionization of lead in sulfate or nitrate solution is rapid. In the case of nitrate in the frequency range studied (from 20 Hz to 100 kHz) the boundary impedance corresponds to the Warburg diffusion impedance [42], the value of which varies regularly with the concentration of Pb^{2+} ions in the solution. The rate of the electrochemical reaction cannot be determined from these data, but its lower limit can be estimated. Calculations show that in 10^{-3} N lead nitrate solution the exchange current i_0 satisfies the inequality $i_0 \geq 0.5 \text{ A/cm}^2$. Introduction of 1,5-dihydroxynaphthalene and of the expanders BNF and tanning agent No. 4 into the solution alters the character of the frequency dependences of the impedance components. In presence of these organic substances the electrical behavior of the lead-solution boundary is described satisfactorily by the equivalent scheme of Ershler and Randles [43, 44], in which retardation of the electrochemical reaction and charging of the electric double layer are taken into account in addition to diffusion of the potential-determining particles in the solution volume. The exchange currents in presence of the above-named substances were determined by analysis of the frequency dependences. The exchange currents for all three organic substances have fairly similar values, amounting to a few milliamperes in 10^{-3} N lead nitrate solution. The transfer coefficients α were determined earlier [38-41]; the values in the cases of 1,5-dihydroxynaphthalene and BNF are 0.7 and 0.6 respectively. The results of differential-capacity measurements in sodium sulfate solutions with additions of the above surface-active substances indicate that these substances are adsorbed in a wide range of potentials, including the potential of zero charge. These substances are desorbed from the electrode surface at considerable negative charges of the surface but, as in [33], desorption peaks were not obtained on curves for the dependence of the differential capacity on potential. The potential of zero charge of lead in a surface-inactive electrolyte is -0.56 V (S.C.E.) [45]. In sulfuric acid solutions specific adsorption of sulfate ions on lead leads to shift of the potential of zero charge in the negative direction; this shift should increase with increasing concentration of sulfate ions in solution. The region of potentials in which lead behaves as an ideally polarizable electrode in which it is possible to conduct direct studies of adsorption of surface-active substances by capacity measurements, is more than 300 mV on the cathodic side of the range of potentials corresponding to operation of the negative plate of the lead battery.

If an electrochemical reaction occurs on an electrode, data on the electric double layer can be obtained only by analysis of the frequency dependences of the impedance components. With the aid of such analysis it was possible to determine the differential capacity of the double layer at the equilibrium potential of lead under the given conditions in potassium nitrate solutions with additions of lead nitrate and in presence of 1,5-dihydroxynaphthalene and of the expanders BNF and tanning agent No. 4 [38-40]. The decrease of the double-layer capacity determined by this method with increasing concentration of the surface-active substances in solution, and the values of the double-layer capacities themselves in presence of these substances are evident of appreciable adsorption of the substances studied on lead at the equilibrium potential, i.e., in the region of potentials where the electrode is positively charged. This appears to be due to interaction of π electrons in the molecules of the aromatic compounds present in the substances studied with the positively charged electrode surface [9].

The above investigations, conducted with smooth and paste electrodes, provide insight into individual aspects of the complex mechanism of the influence of surface-active organic substances on the discharge and charge characteristics of the negative electrode of the lead cell, but the question of the relation between the structure of organic molecules and their action as expanders, which is the most interesting from the practical standpoint, has received very little attention up to now. Attempts to elucidate this relation were undertaken earlier [48, 49]. Ritchie [48] investigated the influence of more than 150 different individual compounds belonging to various classes. The influence of isomerism was also studied. In selection of individual organic substances preference was given to substances which may be regarded as components of organic molecules present in known effective expanders. Ritchie concluded from the results that the effectiveness of lignosulfonic acid derivatives as expanders both in the first cycles and during repeated cycling is due to the reducing properties of phenolic groups and to the improved solubility of these substances as the result of the presence of sulfo groups.

In our opinion, further work in this direction would make it possible to conduct deliberate selection of organic substances suitable as expanders on the basis of their structural formulas, and to raise the coefficient of utilization of the active material of the negative electrode.

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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].