

A view on chemically synthesized expanders for lead/acid battery negative plates

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Abstract

The mechanism of expander action is reviewed, with special emphasis on the role of its organic constituent and the method by which this constituent is derived from lignin. An alternative material, SYNTAN BNF, is proposed for application as the organic constituent. BNF also increases the overvoltage for gas evolution, which could be of special interest for valve-regulated lead/acid batteries. BNF is compatible with α -oxi-naphtholic acid (AONA), an inhibitor of lead oxidation.

Keywords: Lead/acid batteries; Negative plates; Expanders; SYNTAN BNF

1. Background to expander action

The active mass of the spongy negative electrode can lose its operational ability relatively quickly, particularly at low temperatures, high-rate discharges and high acid concentrations. This decline in performance is attributed to passivation of the electrode and to recrystallization and shrinkage of the spongy lead.

During anodic polarization (discharge), the surface of the negative electrode is covered uniformly by a layer of lead sulfate. The latter has a very limited solubility in dilute sulfuric acid, i.e., 3.5×10^{-6} M PbSO_4 [1]. As a result, a supersaturated solution is formed near the electrode surface. The lead sulfate passivates the spongy lead and hinders the anodic (charging) process of the electrode.

Lead sulfate deposits as a tight and impenetrable film that results in 'sintering' of the negative active-material and, thereby, causes a reduction in the volume of the mass. The change in capacity by sintering occurs faster than the change in the 'true' surface area, for example, a tenfold decrease in the first parameter is accompanied by only a fivefold decrease in the second [2]. From measurements of double-layer capacitance, it has been shown [3] that the surface area of a negative electrode, without anti-shrinkage additives, is decreased to 60% of its initial value after only 12 charge/discharge cycles. Similarly, Simon et al. [4] found that unformed negative active-material had a surface area of $0.82 \text{ m}^2 \text{ g}^{-1}$ which then dropped to $0.23 \text{ m}^2 \text{ g}^{-1}$ at the end of the formation charge.

Negative plates appear to need expansion to regenerate the essential pore structure or, to be more precise, to prevent shrinkage that causes excessive loss in capacity. This problem is ameliorated by introducing additives to the negative paste. Logically, these additives are called 'expanders'. This term covers a combination of three types of agent: (i) carbon black; (ii) barium sulfate, and (iii) organic compounds that are typically represented by derivatives of lignin [5].

Finely-divided 'carbon black' was originally added to maintain the conductivity of the spongy lead as the deposited amount of highly-resistant lead sulfate increases during discharge. More importantly, carbon black has a lower hydrogen overpotential than spongy lead [6]. Thus, during charge, hydrogen gas accumulates around the carbon particles and causes a mild expansion of the spongy lead.

The mechanism of barium sulfate has been the subject of several hypotheses. Most probably, when first employed as an expander, the complexity of its mechanism was not fully understood. More likely, barium sulfate was used because of its almost complete insolubility in sulfuric acid, its chemical inertness, and its ready availability. It is generally agreed that barium sulfate is beneficial as a crystallization seed for the formation of lead sulfate on discharge; the two compounds are isomorphous. The application of barium sulfate in negative plates has proved to be one of the major breakthroughs in lead/acid battery technology.

Barium sulfate was widely investigated in Russia in the 1950s by Lorenz [6]. His work showed that sulfates with the same isomorphous structure (such as PbSO_4 , BaSO_4 , and

SrSO_4) and rhombic lattice are the only ones to be effective as expander materials. When highly dispersed, these compounds form numerous centres of crystallization (i.e., nuclei) for the PbSO_4 produced during discharge. Thus, PbSO_4 crystallization on the lead crystals is restrained. A sulfate-free internal surface is preserved in the lead electrode (BET surface area $\sim 0.5 \text{ m}^2 \text{ g}^{-1}$), and the local current density remains at a low value. These findings are in agreement with the results of Willinganz [7]. Other investigations have been reported by Kabanov [1,2]. Note, for an excellent review of research conducted on expanders see Ref. [8].

The most valuable component of the three-part 'expander', particularly in battery service at cold temperatures, is the 'organic component'. For simplicity, this component is termed the organic expander (OE). Its importance was discovered by accident. At the beginning of this century, the separation between the positive and negative plates usually consisted of a thin piece of wood. At that time, it was not recognized that the wood insulator also contained a chemical that had a pronounced beneficial effect on the performance of batteries at both low temperatures and high-discharge rates.

When Willard, founder of Willard Storage Company in the USA, developed an automated plate-drying machine for the production of dry-charged plates, the wet wooden separators could no longer be used and, consequently, were replaced by 'tread rubber' substitutes. The change resulted in battery failures in the colder, northern parts of the USA. After several false starts in battery companies around the world, the problem was solved by digesting wood sawdust in a 72 wt.% H_2SO_4 solution (or similar technology) and adding the residual mass to the negative paste. The same process was used in the paper industry where, during the treatment of wood with 72 wt.% H_2SO_4 , the cellulose was dissolved out and lignin left behind. Lignin found its application in the battery industry in the mid-1920s, but was then superseded by humic and lignin sulfonic acid products. The pattern for the future development of paper industry by-products as additives to batteries was established with the issue of *US Patent No. 2 371 137* in 1949 [9].

Ritchie [10] reviewed the state-of-the-art of OEs in 1947. Not much has changed during the past 50 years, but the hope of finding, or developing, a pure chemical compound with superior expander properties has always been a goal of the battery industry.

The chemistry of lignosulfonates is very complex. They are dissolved in the spent sulfite pulping liquor along with a variety of carbohydrate compounds. The latter are primarily formed by degradation of the hemicellulose components of wood. The chemical composition of hemicellulose varies considerably both with the method of preparation and with the species of tree. The latter affects the proportion of sugars, e.g. glucose, mannose, galactose, xylose, arabinose and rhamnose, in the final product. These sugars usually account for 20 to 25% of the solids in the total spent sulfite liquor [11]. Control of the carbohydrate fraction of lignosulfonate to produce a consistent product is very important, but it is a difficult

task. Several sulfonate derivatives of lignin with surfactant properties are widely used as OEs, for example: Vanisperse, Manisperse, Maracel, Lignosol, Reax, Vanine and Indulin.

Because of its surfactant properties, the OE can be adsorbed on the spongy lead, as well as on the surface of the lead sulfate crystals that are formed during discharge. In both cases, the crystal growth is inhibited by the expander during the dissolution/precipitation process. Without expander, the discharge process creates new centres of crystallization for the lead sulfate on the free sites of the metal until all of the surface is covered with a thick layer of sulfate.

The difference in size of PbSO_4 crystals, with and without OE, has been examined by scanning electron microscopic (SEM) analysis [4]. With no OE present, the lead crystals adsorbed on the lead are quite large in diameter and are covered by the lead sulfate product. Accordingly, the crystals do not reduce completely to lead during the charging process and, thus, prevent the remaining lead from reacting. As a consequence, the negative electrode has low capacity and poor cycle life.

The basis for the prevention of particle coarsening by recrystallization, or sintering, seems to be related to a lowering of the surface energy by the adsorption of additives. This behaviour can be expressed as [12]:

$$\sum \sigma_i S_i \rightarrow \min \quad (1)$$

where σ_i and S_i are the specific surface energy and specific surface area of a crystal site, respectively. Adsorption of OE on the lead crystals decreases the free surface energy due to a reduction in the surface tension. This means that the formation of coarser crystals is energetically less favourable in the presence of the expander. Rather, smaller and more loosely-packed lead crystals are produced and, thereby, the morphology is changed. In this way, the OE prevents the formation of dense, insulating layers of sulfate. Crystallization of the lead sulfate occurs not on the metal but beyond the layer of adsorbed OE particles, and is loosely connected with the lead surface.

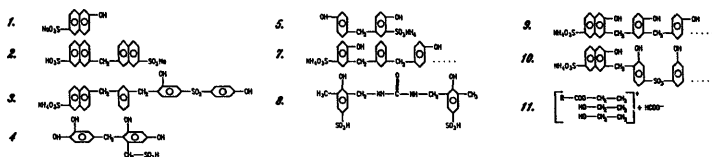
The change in crystal size and morphology has been confirmed by SEM studies [4]. In the presence of OE, it was found that crystals of smaller size, with a sphere-like shape, were connected together in a dendritic, conductive network that inhibited passivation of the negative electrode. The delayed passivation of the lead electrode in the presence of OEs has been widely reported [4,6–8,12–24].

It has been shown that adsorption of OE on spongy lead or PbSO_4 crystals exerts opposite effects with respect to passivation of the electrode. OE adsorption on lead produces an activation effect, but OE adsorption on PbSO_4 can result in passivation of the negative electrode due to increased supersaturation of the solution [1,25].

The selection principles for an effective OE are still unclear. In early studies [6], the following relationship was obtained from general considerations:

Table 1

Code number	SYNTAN	Description
1	SHEFFER SALT	
2	SYNTAN NK	Product of condensation of naphthalene sulfonic acid and formaldehyde (CH ₂ O)
3	SYNTAN NKS	Same as #2, with addition of organic acids after neutralization by NH ₄ OH
4	SYNTAN-1	Product of ω-condensation of phenol or its homologs with CH ₂ O, treated by Na ₂ SO ₃ and NaOH in water media
5	SYNTAN-2	Product of phenol condensation with CH ₂ O, treated by concentrated H ₂ SO ₄
6	SYNTAN-3	Product of phenol condensation with CH ₂ O and dispersion in lignosulfonic acids
7	SYNTAN-4	Product of condensation of blended phenols, sub-product of carbonization of coal, with β-naphthol-sulfonic acid and CH ₂ O
8	SYNTAN-5	Product of condensation of sulfated cresol with CH ₂ O and CO (NH ₂) ₂
9	SYNTAN BNF	Same as SYNTAN #4, but instead of blended phenols, chemically synthesized phenols are used
10	SYNTAN BNS	Product of condensation of sulfonized β-naphthol with di-oxi-diphenylsulfon
11	CATIONIC SYNTAN	Salt of monoether of high-molecular fatty acids and triethanolamine



$$-\frac{\partial \sigma}{\partial m} = f(Z, P, M, R) \quad (2)$$

According to this dependence, the adsorption of any particle on an electrode ($-\partial \sigma / \partial m$) increases with increase in the charge (Z), molecular weight (M), specific refraction (R), and dipole moment (P). In the case of OE adsorption, the electrode surface and the adsorbed OE particles have opposite polarity. This is an important criterion in OE selection. Lead is positively charged against the electrolyte at the equilibrium potential of the negative electrode (-0.35 V). Therefore, anions of high molecular weight or negative colloidal particles are preferentially adsorbed.

Unfortunately, even though a large number of organic compounds have been chosen in accordance with the above-mentioned principles, there is still a very limited understanding of OE action. Indeed, despite some strenuous attempts [18], no dependable test has been devised to evaluate OE activity. Moreover, the structures of the selected organic compounds remain ill-defined. Therefore, it is necessary to search for new chemically stable and well-defined substances that can serve as effective OEs.

2. Development of SYNTAN-based organic expanders

In Russia, in the late 1960s, the first attempt was made to find a substitute for the lignosulfonates in common use as OEs [26,27]. The main reason for this work was the incompatibility of lignosulfonates with α-oxi-naphtholic acid

(AONA) [19,28] which, at that time, was widely used as an inhibitor of lead oxidation [29].

Russian technology for producing dry-charged negative plates was based on the principle of drying in a conveyor tunnel oven, with no vacuum. This could only be achieved by application of AONA to prevent the formed negative plates from being oxidized during the air-drying stage [19,28–31].

The search for an OE that was compatible with AONA was focused not only on lignosulfonates specifically designed for that purpose (Sunil, etc.) [32], but also on products that contain naphthalene groups with a structure similar to AONA. Eventually, the naphthalene-based products of the tannin industry, SYNTANS, were identified as suitable replacements for lignosulfonates [19,26–34].

The raw materials in SYNTANS production are first processed through a primary synthesis reaction in order to increase the number of aromatic nuclei in the molecule and to achieve solubility in water, i.e.,



where Ar is the aromatic radical. This intermediate product is subjected to repeated treatment with formaldehyde, and then neutralized to pH: 3.0–3.5 [35].

The aromatic groups (as phenols) can also react with bisulfite, instead of sulfuric acid, i.e.:



This reaction is called ω-sulfonation (or methylsulfonation).

Table 2
Initial capacity of negative electrodes doped with various SYNTANS. Capacity given in terms of discharge time (h)

SYNTAN (code number)	Cycle number			
	1	3	5	11
9	4.50	6.00	7.42	8.18
10	4.35	6.83	6.92	7.83
3	4.30	5.87	6.83	7.67
4	4.02	5.75	6.35	6.70
5	4.20	5.80	6.25	7.18
6	4.03	5.63	6.00	6.83
7	4.53	6.03	7.25	8.00
8	4.97	4.70	6.00	6.88

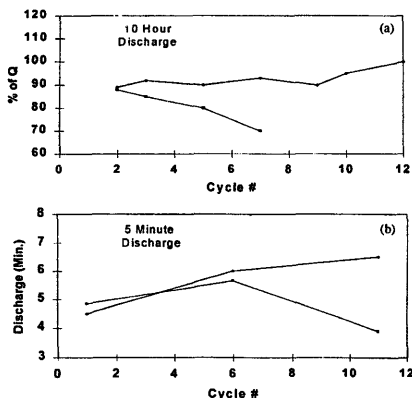


Fig. 1. Limitation of capacity in presence of lignosulfonate in combination with AONA: (●) lignosulfonate, and (■) lignosulfonate + AONA.

The SYNTANS that were subjected to evaluation are listed in Table 1 [19]. The factors specified for investigation focused on: (i) products with different lengths of organic chain (#1, #2, #3); (ii) the charge polarity (#11); (iii) products of naphthalene condensation with formalin (#2, #3, #10); (iv) products of phenol condensation with formaldehyde (#4-#9); (v) products subjected to ω -sulfonation (#4); (vi) products of phenol condensation with formaldehyde and dispersed in lignosulfonic acids (#6); (vii) products of condensation of formaldehyde and β -naph-

thol-sulfonic acid with blended phenols (#7) or chemically synthesized phenols (#9). Most of the SYNTANS were tested as single additions to negative pastes and at similar concentrations, or in combination with AONA.

The experiments were conducted in small Plexiglass cells with pasted electrodes of 2 mm thickness. The cell assembly comprised a lead test electrode between two counter positive electrodes in a large excess of sulfuric acid. The performance of some of the additives was examined in practical batteries, especially under 'cold-cranking' test conditions at -18°C .

Negative electrodes doped with various SYNTANS generally maintained high electrical capacity on cycling (Table 2). The only exceptions were the cationic SYNTAN #11, and SYNTANS #1 and #2 with short chains (Table 2).

Some of the tested SYNTANS, however, were not compatible with AONA (i.e., #2, #3, #5, #12) and lowered the capacity in a manner similar to the effect of AONA in combination with the lignosulfonates (Fig. 1). This could be due to the method used for the SYNTAN synthesis. For example, free phenols not condensed with formaldehyde, after combination with AONA radicals, could cause over-saturation with the insoluble groups and, consequently, could result in passivation of the negative electrode. BNF, BNS and #4 exhibited the best compatibility with AONA (Table 3).

In order to investigate the dependence of SYNTAN activity on the level of condensation achieved during its preparation (which depends on the amount of formaldehyde that is able to combine with the phenol and naphthalene groups), the following three products of SYNTAN BNF with different degrees of condensation have been tested [19]:

1. The amount of formaldehyde in the recipe was increased by 20% with a corresponding decrease in the amount of phenol (deep condensation of both group types).
2. The amount of phenol was decreased by 20%, with the amount of formaldehyde kept in accordance with the recipe (balance is shifted in the phenol direction).
3. The amounts of both phenol and formaldehyde were decreased by 20% (balance is shifted in the naphthalene direction, with a corresponding decrease in molecule size).

From Fig. 2, it is clear that the electrode capacity depends strongly on the level of condensation of the phenol and naphthalene groups. The best results are given by #1 which has the highest level of condensation.

Table 3
Capacity of 6ST-55 batteries at -18°C with various SYNTANS and their combination with AONA. Capacity given in terms of discharge time (h)

Cycle number	Additive (s)						
	Vanisperse	BNF	BNF + AONA	BNS	BNS + AONA	#4	#4 + AONA
4	3.25	3.62	3.50	2.93	3.08	3.37	3.47
8	4.00	3.97	4.00	3.42	3.25	3.63	3.58
142	2.42	3.07	3.30	2.92	2.67	2.97	3.17

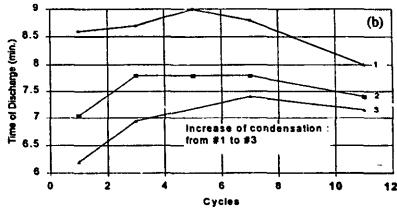
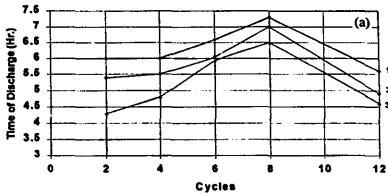


Fig. 2. Capacity of the negative electrode vs. level of condensation of SYNTAN BNF.

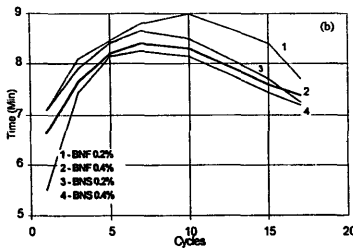
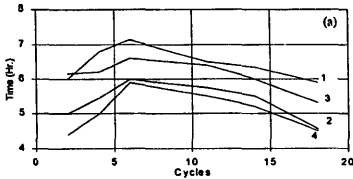


Fig. 3. Limitation of capacity with increase in SYNTAN concentration.

The dependence of electrode capacity on the free-radical groups corresponds to the concentration of the added SYNTAN. From Fig. 3, it is evident that an increase in the concentration of BNF or BNS, from 0.2 to 0.4 wt.%, results in a decrease in capacity. This can also be explained by the passivating effect of the free radicals.

Even though SYNTANS BNF, BNS and #4 displayed similar results in electrical tests, a higher chemical stability of the original materials used in the synthesis of BNF (chemically synthesized phenols) was taken as the main consider-

ation. After further testing in batteries (Fig. 4 and Table 3), SYNTAN BNF was proposed for practical application in Russian Patent No. 183 251 in 1965 [27]. It continues to be used in Russian battery plants.

In addition to its utility as an expander, SYNTAN BNF also impedes the kinetics of hydrogen evolution and shows a strong tendency to inhibit gas evolution during self-discharge testing (Figs. 5 and 6) [19]. This feature could be used to advantage in valve-regulated lead/acid batteries.

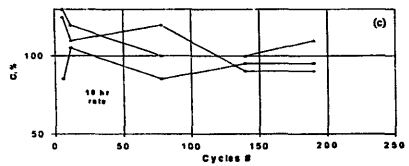
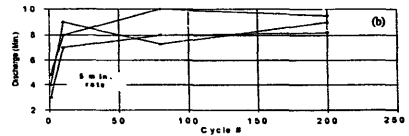
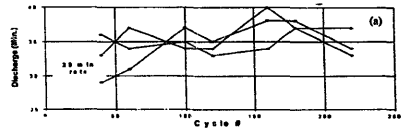


Fig. 4. Cycle life of batteries with different organics in the negative plates: (●) BNF, 0.25%; (■) BNF, 0.25% + AONA, and (▲) Vanisperse, 0.4%.

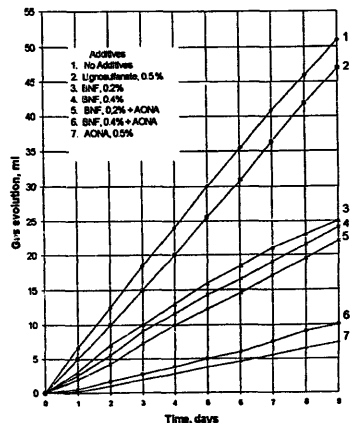


Fig. 5. Gas evolution in the presence of SYNTAN BNF and AONA.

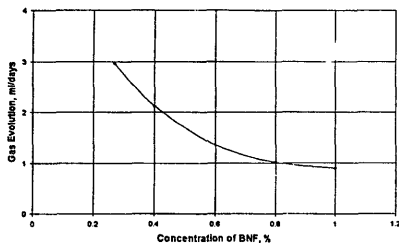


Fig. 6. Gas evolution as a function of added amount of SYNTAN BNF.

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References

- [1] B.N. Kabanov, *Proc. 3rd Conf. Electrochemistry, Moscow, Russia, 1953*, p. 138.
- [2] B.N. Kabanov, *Dokl. Acad. Nauk, Moscow, USSR, 31* (1942) 582.
- [3] N.G. Kuznetsova, *Dissertation*, Leningrad, Russia, 1940, p. 9.
- [4] A.C. Simon, S.M. Caulder, C.P. Wales and R.L. Jones, US Naval Research Laboratory, *Rep. No. 4751*, for US Department of Energy, 1982.
- [5] G.W. Vinal, *Storage Batteries*, Wiley, New York, 1947; Gosenergoisdat, Moscow, Leningrad, 1960.
- [6] A.K. Lorenz, *Dissertation*, Leningrad, Russia, 1953.
- [7] E. Willinganz, *Trans. Electrochem. Soc.*, **92** (1947) 281.
- [8] J. Burbank, A.C. Simon and E. Willinganz, *Adv. Electrochem. Electrochem. Eng.*, **8** (1970) 157.
- [9] C. Harmon and J.A. Orsino, *US Patent No. 2 371 137* (Mar. 1945).
- [10] E.J. Ritchie, *Trans. Electrochem. Soc.*, **92** (1947) 227; *J. Electrochem. Soc.*, **100** (1953) 53.
- [11] F.E. Brauns, *The Chemistry of Lignin*, Academic Press, New York, 1952; K.V. Sarkanen and C.H. Ludwig, *Lignin*, Wiley, New York, 1971; E. Sjöstrom, *Wood Chemistry*, Academic Press, New York, 1981.
- [12] M.A. Dasoyan and I.A. Aguf, *The Lead Accumulator*, Asian Publication House, Bombay, 1968, pp. 44; 78.
- [13] K. Peters, A.I. Harrison and W.H. Durant, *J. Power Sources*, **2** (1970) 1.
- [14] E. Willinganz, *J. Power Sources*, **5** (1975) 43.
- [15] P.J. Mitchell and N.A. Hampson, *J. Power Sources*, **8** (1982) 197.
- [16] T.F. Sharpe and R.S. Connel, *J. Appl. Electrochem.*, **17** (1987) 789.
- [17] P. Ekdunge, K.V. Ribalka and D. Simonsson, *Electrochim. Acta*, **32** (1987) 666.
- [18] B.K. Mahato, *J. Electrochem. Soc.*, **127** (1980) 1679; **128** (1981) 1416.
- [19] G.I. Manoim-Aidman, *Dissertation*, Institute of Technology, (Leningradskiy Technologicheskiiy Institute imeni Lensovieta), Leningrad, USSR, 1971.
- [20] A.A. Azim and A.A. Ismael, *J. Appl. Electrochem.*, **4** (1974) 351.
- [21] D. Pavlov, and V. Iliev, *J. Power Sources*, **7** (1981) 153; D. Pavlov and S. Ignatova, *J. Appl. Chem.*, **17** (1987) 715.
- [22] J.R. Pierson, P. Gurlusky, A.C. Simon and S.M. Caulder, *J. Electrochem. Soc.*, **117** (1970) 1463; **121** (1974) 463.
- [23] C.P. Wales, S.M. Caulder, A.C. Simon and S.M. Caulder, *J. Electrochem. Soc.*, **128** (1981) 236.
- [24] M.P. Brennan and N.A. Hampson, *J. Electroanal. Chem. and Interfacial Electrochem.*, **48** (1973) 465; **54** (1974) 263.
- [25] E.G. Yampolskaya and B.N. Kabanov, *Sov. J. Appl. Chem.*, **37** (1964) 2530; E.G. Yampolskaya, M.I. Ershova, I.I. Astakhov and B.N. Kabanov, *Electrochimia (Moscow)*, **2** (1966) 1327.
- [26] Y.B. Kasparov and E.G. Yampolskaya, *USSR Patent No. 137 556* (1961).
- [27] V.V. Novoderezhkin, G.I. Manoim-Aidman, I.I. Pucheglazova, E.G. Yampolskaya, I.A. Smirnova, S.A. Kuraytis and S.K. Golubeva, *USSR Patent No. 183 251* (1965).
- [28] G.I. Manoim-Aidman, V.V. Novoderezhkin, I.I. Pucheglazova and E.S. Israileva, *Sb. Rab. Chim. Istochnikam Toka 1* (1966) 57 (Collected papers on electrochemical power sources).
- [29] R.H. Greenburg and J.A. Orsino, *US Patent No. 2 759 037*.
- [30] G.I. Manoim-Aidman, M.A. Dasoyan, V.V. Novoderezhkin and I.I. Kruglova, *Sb. Rab. Chim. Istochnikam Toka*, **5** (1970) 44; G.I. Manoim-Aidman, V.V. Novoderezhkin, I.I. Kruglova and M.A. Dasoyan, *Sb. Rab. Chim. Istochnikam Toka*, **7** (1972) 22 (Collected papers on electrochemical power sources).
- [31] V.V. Novoderezhkin, G.I. Aidman, E.P. Bordt and Y.A. Belkov, **2** (1978) 123 (Collected papers on electrochemical power sources).
- [32] G.I. Aidman, Y.V. Litlov and E.G. Yampolskaya, *Electrotech. Ind. (Moscow)*, **63** (1978) 5.
- [33] G.I. Manoim-Aidman, M.A. Dasoyan and V.V. Novoderezhkin, *J. Appl. Chem. (Moscow)*, **44** (1971) 799.
- [34] G.I. Manoim-Aidman, M.A. Dasoyan and V.V. Novoderezhkin, *Electrochimika (Moscow)*, **42** (1971) 52.
- [35] A.N. Michailov, S.K. Golubeva, S.A. Kuraytis, S.I. Smirnov, X.S. Toporovskaya, N.B. Filippova and P.Y. Frenkel, *Synthesized Tannins*, Light Industry, Moscow, 1967.