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THERMAL INVESTIGATION OF THE MANUFACTURE OF ACTIVE SUBSTANCE FOR LEAD STORAGE BATTERIES

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ABSTRACT

The preparation of the active substance of lead storage batteries and the experimental conditions have been investigated with a derivatograph. In the course of this work, complemented by X-ray diffraction investigations, the manufacturing processes could be partly cleared, and thermoanalytical methods could be applied for their control. It has been established that a tribasic sulfate of the composition $3PbO \cdot PbSO_4 \cdot nH_2O$ is formed on mass mixing, and the value of "*n*" can be influenced by changing the experimental conditions.

1. INTRODUCTION

Although more than 110 years have elapsed since the discovery of storage batteries, and today they are manufactured already on modern, automatic production lines, there is still no uniform, unequivocal theoretical explanation for their operation. Only very few publications on batteries in the literature deal with manufacturing processes. Most papers describe the operation and properties of finished batteries. Neither give fundamental works[1–4] dealing with batteries or their production, detailed data or explanations on the single manufacturing processes. Moreover the chemical reactions taking place in this process are discussed very rarely. This can be explained only partly by trade secrets. Actually there are many unsolved problems and many assumptions in connection with the chemical processes involved.

The processes, basic substances and semi-finished products of battery manufacture almost offered an opportunity for the extension of the use of thermal methods to the control and investigation of the manufacturing processes. The investigation of the manufacturing process is made easier by the high purity of the substances, which is needed in the manufacture of electrochemical power sources.

The derivatograph was chosen for the investigations. To our knowledge, in the battery and dry cell manufacturing industry, TA measurements have been used so far only in connection with the manufacture and materials of dry cells and alkaline batteries. However, in the field of the manufacture of acid/lead/batteries only the paper of Bazalgette[5], published in 1960, reports on TG measurement, involving the investigation of lead dust and plates with a Chevenard thermobalance, from which simple conclusions were drawn, as a completion of other measurements.

On the basis of the investigation with a derivatograph of the semi-finished products obtained in the single phases of plate manufacture, conclusions can be drawn also on the chemical reactions, taking place in the course of the manufacturing processes. Thermal measurements were complemented by classical analysis and X-ray diffraction in order to support the conclusions drawn. We carried out experiments in the field of lead battery manufacture. However, the present paper reports only on the investigations relevant to the manufacture of the active substance (paste mixing) of the positive electrode of self-starting batteries for motocars.

2. SURVEY OF LITERATURE

The reaction taking place during mass mixing is explained by most authors[2,3,6] by the most evident equation:

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O \qquad (1)$$

Toelle and Von Hofe[7] assumed on the basis of their experiments carried out in 1905 that on the slow addition of H_2SO_4 to PbO under continuous stirring, a mixture of three basic sulfates is formed. The constituents of the mixture are $PbO \cdot PbSO_4 \cdot H_2O$, $3PbO \cdot 2PbSO_4 \cdot 3H_2O$ and $PbO \cdot 2PbSO_4 \cdot H_2O$. Discussing the PbO–H_2SO_4 pastes, Takagaki[8] established that the mass used in battery plates consists in addition to PbO with water of basic $PbSO_4$ ($4PbO \cdot PbSO_4$) containing water.

Burbank[9] states in his paper, dealing with the anodic oxidation of basic sulfates, that the mass is a composite mixture, consisting of unreacted lead oxide, one or more basic sulfates, possibly basic carbonate, and hydrated lead oxide. Among the basic sulfates, the following can be most often found in the mass: $PbO \cdot PbSO_4$; $3PbO \cdot PbSO_4 \cdot H_2O$ and $4PbO \cdot PbSO_4$.

With reference to the research work of Mrgudich[10], Vinal[1] presumes also the formation of tetrabasic sulfate on mixing lead oxide with sulfuric acid. According to his investigations, the tribasic sulfate appears only, when the quantity of sulfuric acid is about three-fold. Lander[11] reports that $PbO \cdot PbSO_4$ and $3PbO \cdot PbSO_4 \cdot H_2O$ are also present besides $4PbO \cdot PbSO_4$. According to Simon[12], $4PbO \cdot PbSO_4$ can be formed only if the temperature is controlled during mass mixing and drying, but it is converted more difficultly to the dioxide in the course of later operations. MacInnes[13] presumes also that $4PbO \cdot PbSO_4$ is formed only on the discharge of the battery plates, together with several other basic sulfates.

Schneider[14] presumes that PbO with sulfuric acid forms various basic sulfates, the composition of which depends on the process used. According to Schneider, the essence of the process taking place is as follows:

$$2PbO + H_2SO_4 + nH_2O \rightarrow (PbOH)_2SO_4 \cdot nH_2O \qquad (2)$$

i.e., monobasic sulfate, containing water $PbO \cdot PbSO_4 \cdot nH_2O$ is formed.

The data in the literature given above and summary works on lead compounds[15,16] presume the existence of the following basic sulfates: +$PbO \cdot PbSO_4$; +$PbO \cdot PbSO_4 \cdot H_2O$; +$PbO \cdot PbSO_4 \cdot nH_2O$; $2PbO \cdot PbSO_4$; +$3PbO \cdot PbSO_4$; +$3PbO \cdot PbSO_4 \cdot H_2O$; $3PbO \cdot PbSO_4 \cdot nH_2O$; +$4PbO \cdot PbSO_4$; $PbO \cdot 5PbSO_4$; $2PbO \cdot 3PbSO_4$; +$3PbO \cdot PbSO_4 \cdot 3H_2O$; +$3PbO \cdot 2PbSO_4 \cdot 3H_2O$; +$PbO \cdot 2PbSO_4 \cdot H_2O$. From these basic sulfates, those which according to data in the literature are presumed to be present alone or together in the mass, have been marked with +.

2.1 The density and quantity of sulfuric acid used for the preparation of the mass

Today, the plates or masses of motorcar starting batteries are prepared already after aqueous premixing with sulfuric acid of 1.4 g ml^{-1} density, though in some factories premixing with dilute sulfuric acid of 1.1 g ml^{-1} density is used instead of aqueous premixing which is then followed by mixing with sulfuric acid of 1.4 g ml^{-1} "normal" density. In spite of this, the use of sulfuric acid of 1.4 g ml^{-1} density is to be considered as general practice. This is also mentioned in the scarce data in the literature[14,17-19]. The use of sulfuric acid of this density is based on practical experiences. This relatively more concentrated sulfuric acid is needed on the one hand because of the stricter requirements to be met by starting batteries, and on the other hand, on account of the more rigid and harder masses, necessary for mechanical pasting. A further increase in density would worsen certain properties of the plates, and would also cause difficulties in the homogeneous mixing of sulfuric acid into the mass. The quantity of sulfuric acid used in mass mixing varies both in practice and in the literature within wider limits than its density.

Taking the quantity of sulfuric acid, calculated according to reaction (1) as 100, the quantity of sulfuric acid added is expressed in percent. When the sulfuric acid quantities used in practice are determined with this mode of expression, it can be established that although they rather vary in the prescriptions used by the single battery factories, they are generally between 6 and 15%. On the other hand, some researchers recommend mass preparation, starting from mixtures with a basic sulfate content between 15 and 25%[20-23].

It should be noted that the quality of lead dust, the methods of drying and formulation are also pertinent to the various manufacturing prescriptions. Only the harmony of these prescriptions in their totality ensures the development of a good active substance in the plate.

The effect of the change in quantity of sulfuric acid has been observed. However, the literature does not give theoretical conclusions or unequivocal explanations. Though Takagaki[8,24] and Mrgudich[10] carried out experiments with $PbO + H_2SO_4$ mixtures containing various quantities of sulfuric acid, the results reported do not make possible unequivocal conclusions, because certain data are lacking. Moreover, the presence of basic sulfates of different composition in the mass is presumed by the two authors. The literature contains only sporadic data on the quantity of sulfuric acid used for mass mixing. Greenburg[17] gives 14.0%, Schneider[14] 14.3% as the optimal sulfuric acid quantity.

2.2 Thermal decomposition processes of basic sulfates

In the investigations with a derivatograph, the basic sulfates in the mass mixture undergo various thermal decomposition processes, the knowledge of which is indispensable for the evaluation of the measurements. Several authors examined the thermal decomposition of certain basic sulfates, but data on the decomposition of basic sulfates containing water are very scarce. Most publications deal only with processes of the PbO–$PbSO_4$ system proceeding above 200 and 400°C, respectively.

On heating $PbSO_4$, decomposition begins at 637°C[25], and at 705°C $6PbO \cdot 5SO_3$ is formed. On further heating, at 962°C, $2PbO \cdot SO_3$ is formed[25]. According to Takagaki[8] the β-form of basic $PbSO_4$ changes to the γ-form on heating ($4PbO \cdot PbSO_4$), which is then further decomposed at 630°C to $2PbO \cdot PbSO_4$. According to Simon[12], $4PbO \cdot PbSO_4$ is formed at 70°C, while $2PbO \cdot PbSO_4$ is stable only above 450°C. Kellogg and Basu[26] found that the decomposition of $2PbO \cdot PbSO_4$ occurs at 616°C. According to Landner[27], the dibasic sulfate is decomposed at 450°C into two parts, monobasic and tetrabasic sulfates, Esdaile[28] attributes the DTA peak at 450°C to the allotropic transformation of the dibasic sulfate below 631 °C. This was first indicated by Schenk and Rassbach[29]. According to Jaeger and Germs[30], the decomposition of dibasic sulfate yields mono- and tribasic sulfates in a quantity of 50 to 75%. However, this assumption is not supported by others. Moreover, they even agree on the finding[31] that tribasic sulfate is unstable in this temperature range.

It can be seen from the aforesaid that the results of the studies dealing with PbO–$PbSO_4$ systems differ considerably. Therefore, Tridot et al.[31] attempted to follow the changes of this system between 400 and 900°C by thermal analysis, radiocrystallographic investigations and high temperature X-ray diffraction investigations. They summarize the single fundamental research works in the literature[27,28] as follows: In the temperature range from 400 to 900 °C, the existence of three basic sulfates: $PbO \cdot PbSO_4$, $2PbO \cdot PbSO_4$ and $4PbO \cdot PbSO_4$ is verified by the experiments.

The "low-temperature" α-form of the dibasic sulfate, $2PbO \cdot PbSO_4$, is transformed at 450°C into a "high-temperature" β-modification. The β-form is not stable at this temperature, its decomposition yields $PbO \cdot PbSO_4$ and $4PbO \cdot PbSO_4$, which at 620°C forms again "high-temperature" dibasic sulfate of the β-form. On heating lead sulfate, at 840°C an allotropic transformation takes place. According to the experiments of the authors, decomposition begins at 760°C, however, TG measurements showed it is stable up to 1050°C.

The monobasic sulfate did not show changes in this temperature range.

The tetrabasic sulfate too, begins to decompose at about 800°C. During the manufacture of the plates, even the highest temperature does not exceed 100°C, and during drying 200°C. Thus, data in the literature, although they do not contribute to the interpreation of the manufacturing process, were very helpful in the evaluation of our TA investigations.

The TG investigation of the single phases of battery manufacture is so far only mentioned by Bazalgette[5] in 1960, in connection with the comparative investigation of semi-finished and finished products, prepared from two different lead dusts. Here, lead dust, and pasted and dried plates are investigated on a Chevenard balance. However, mass mixing has not been investigated by Bazalgette.

3. RESULTS AND CONCLUSIONS

For the preparation of the experimental mass mixtures, the so-called "lead dust", used in storage battery manufacture, has been used, which is actually a mixture of lead(II) oxide and metallic lead dust.

TA measurements were carried out with a Paulik–Paulik–Erdey derivatograph Model Orion-Gyem No. 676[32].

Experimental conditions of the measurements were as follows: Weight of sample: about 500 mg; reference substance: α-Al_2O_3; heating rate: 10 °C min^{-1}; crucible: corundum[33]; atmosphere: air.

A diffractometer manufactured by Rigaku-Denki Ltd. Co. was used for X-ray diffraction measurements. Measuring parameters used: CuK_α, 32 kV, 24 mA.

3.1 Investigation of the mass mixture

According to our experiences in mass mixing emphasized also by some sources in the literature[14], the mixed masses have an alkaline pH. Thus, sulfuric acid added to the mass is used up (in its total quantity) for the formation of basic sulfates, since on the basis of practical experiences only a ratio of the quantity of sulfuric acid, calculated on the basis of eqn (1) is admixed in the manufacture for mass preparation.

Laboratory experiments were undertaken to obtain information on the composition of the mass, and on the effect caused by changing the density and the quantity of sulfuric acid used.

In the preparation of the single mixtures, it was attempted to approach as far as possible the circumstances and the technological operations of mass mixing in the plant. The experiments and the conditions of mass mixture preparation made it also possible to draw quantitative conclusions.

In the course of the experiments, first an answer was to be found on the composition and the main constituents of mass mixtures. After the admixture of water with lead dust (premixing), the mixture contains in essence PbO, Pb and H_2O, and possibly loosely bound $PbO \cdot nH_2O$ components of non-crystalline structure may be present.

The derivatograms of the mass mixtures, whether recorded under plant or laboratory conditions, show the same course. Figure 1 shows the thermoanalytical curves of an experimental mixture. After the loss of water content, an endothermic decrease in weight of about 1% occurs at 240 °C. Subsequently, at about 350 °C, the free lead content of the mass is oxidized, which is manifested by the increase in weight shown by the TG curve. This latter process is exothermic. The small endothermic peak

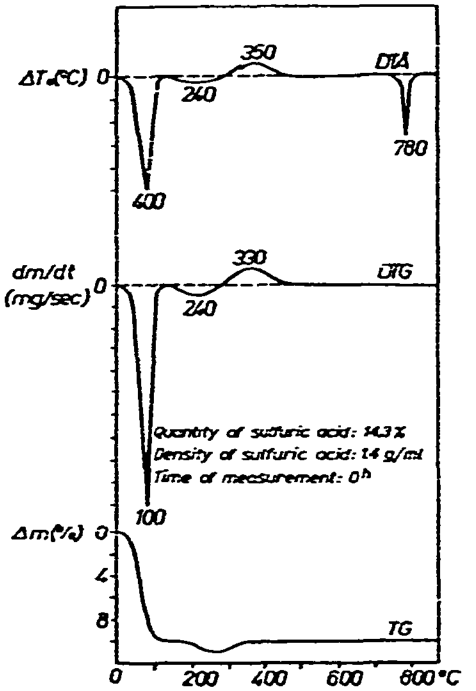


Fig. 1. Derivatogram of experimental mass mixture. Quantity of sulfuric acid: 14.3%; density of sulfuric acid: 1.4 g ml^{-1}; time of measurement: 0 h.

at about 320°C, indicating the melting of unreacted lead, is superposed on this exothermic process.

On the basis of what was said earlier, the decrease in weight at 240°C indicates the decomposition of a basic sulfate or sulfates containing water. It cannot be established from the derivatogram, which of the basic sulfate or sulfates are present. This question was answered by the results of X-ray investigations. On the basis of the investigation of the mass mixtures, only $3PbO \cdot PbSO_4 \cdot nH_2O$ is present in the mixed mass (Table 1), and this does not change during storage.

Basic sulfates of other composition could not be detected in the mass mixtures. In addition to the X-ray diffraction investigation of the mass mixture, the mass mixture heated to 100°C and having lost its water content, and the mass mixture heated to 300°C after the step at 240°C have also been investigated by the "freezing-in" of the test with the derivatograph. Thus, freezing-in took place before and after the decomposition of the basic sulfate. The mass treated at 100°C contained also $3PbO \cdot PbSO_4 \cdot nH_2O$ (see Table 2). From the samples taken at 300°C (Table 3), $3PbO \cdot PbSO_4 \cdot nH_2O$ disappeared, decomposed, and instead the form $4PbO \cdot PbSO_4$ was present. Similarly in the same measurements, besides the red PbO modification the yellow PbO modification appeared. These experiences are not inconsistent with the experimental results of Tridot et al.[14]. Indeed, $4PbO \cdot PbSO_4$ is not formed here by the decomposition of $2PbO \cdot PbSO_4$ above 450°C, but by the decomposition of $3PbO \cdot PbSO_4 \cdot nH_2O$ in the presence of PbO in the course of the experiments.

TABLE 1

RESULTS OF THE X-RAY DIFFRACTION INVESTIGATION OF THE MASS

Quantity of sulfuric acid: 14.3%; density of sulfuric acid: 1.4 g ml^{-1}; time of measurement: 0 h.

d_{hkl}	*Intensity*	*Cryst. phase*
9.8	10	$3PbO\cdot PbSO_4\cdot nH_2O$
6.2	1	$3PbO\cdot PbSO_4\cdot nH_2O$
5.7	3	$3PbO\cdot PbSO_4\cdot nH_2O$
5.02	5	PbO, red
4.9	3	$3PbO\cdot PbSO_4\cdot nH_2O$
4.23	4	$3PbO\cdot PbSO_4\cdot nH_2O$
3.60	2	$3PbO\cdot PbSO_4\cdot nH_2O$
3.25	25	$3PbO\cdot PbSO_4\cdot nH_2O$
3.11	63	PbO, red
2.95	1	$PbO_{1.5}$
2.88	4	$3PbO\cdot PbSO_4\cdot nH_2O$
2.87	1	$PbO_{1.5}$
2.81	16	PbO, red
2.71	6	$3PbO\cdot PbSO_4\cdot nH_2O$
2.51	25	PbO, red
2.43	3	$3PbO\cdot PbSO_4\cdot nH_2O$
2.16	2	$3PbO\cdot PbSO_4\cdot nH_2O$
2.12	1	PbO, red
2.08	3	$3PbO\cdot PbSO_4\cdot nH_2O$
1.99	5	PbO, red
1.95	2	$3PbO\cdot PbSO_4\cdot nH_2O$
1.87	20	PbO, red
1.74	1	$PbO_{1.5}$
1.68	14	PbO, red
1.63	1	$3PbO\cdot PbSO_4\cdot nH_2O$
1.56	8	PbO, red
1.54	15	PbO, red

TABLE 2

RESULTS OF THE X-RAY DIFFRACTION INVESTIGATION OF THE MASS HEATED TO 100°C

Quantity of sulfuric acid: 14.3%; density of sulfuric acid: 1.4 g ml^{-1}; time of measurement: 0 h.

d_{hkl}	*Intensity*	*Cryst. phase*
9.8	15	$3PbO\cdot PbSO_4\cdot nH_2O$
6.2	2	$3PbO\cdot PbSO_4\cdot nH_2O$
5.7	7	$3PbO\cdot PbSO_4\cdot nH_2O$
5.02	5	PbO, red
4.9	4	$3PbO\cdot PbSO_4\cdot nH_2O$
3.23	5	$3PbO\cdot PbSO_4\cdot nH_2O$
3.60	3	$3PbO\cdot PbSO_4\cdot nH_2O$
3.48	2	$PbO_{1.5}$
3.25	31	$3PbO\cdot PbSO_4\cdot nH_2O$
3.11	82	PbO, red
2.95	7	$PbO_{1.5}$
2.88	7	$3PbO\cdot PbSO_4\cdot nH_2O$
2.85	8	Pb

(Table continued on p. 286)

TABLE 2 (*continued*)

d_{hkl}	*Intensity*	*Cryst. phase*
2.81	28	PbO, red
2.71	5	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.51	22	PbO, red
2.50	6	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.43	3	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.16	3	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.08	3	$3PbO \cdot PbSO_4 \cdot nH_2O$
1.99	6	PbO, red
1.95	2	$3PbO \cdot PbSO_4 \cdot nH_2O$
1.87	24	PbO, red
1.74	4	$PbO_{1.5}$
1.68	18	PbO, red
1.63	2	$3PbO \cdot PbSO_4 \cdot nH_2O$
1.56	9	PbO, red
1.54	13	PbO, red

TABLE 3

RESULTS OF THE X-RAY DIFFRACTION INVESTIGATIONS OF THE MASS HEATED TO 300°C

Quantity of sulfuric acid: 14.3%; density of sulfuric acid: 1.4 g ml^{-1}; time of measurement: 0 h.

d_{hkl}	*Intensity*	*Cryst. phase*
8.1	6	$4PbO \cdot PbSO_4$
7.3	2	$4PbO \cdot PbSO_4$
5.89	10	PbO, yellow
5.80	3	$4PbO \cdot PbSO_4$
5.45	2	$4PbO \cdot PbSO_4$
4.25	2	$4PbO \cdot PbSO_4$
3.25	55	$4PbO \cdot PbSO_4$
3.11	40	PbO, red
3.07	64	PbO, yellow
2.95	40	PbO, yellow
2.87	19	$4PbO \cdot PbSO_4$
2.81	5	PbO, red
2.74	8	PbO, yellow
2.65	26	$4PbO \cdot PbSO_4$
2.38	6	PbO, yellow
2.00	7	PbO, yellow
1.96	9	$4PbO \cdot PbSO_4$
1.94	16	$4PbO \cdot PbSO_4$
1.86	5	PbO, red
1.85	4	PbO, yellow
1.82	3	$4PbO \cdot PbSO_4$
1.80	5	PbO, yellow
1.72	19	$4PbO \cdot PbSO_4$
1.64	8	$4PbO \cdot PbSO_4$
1.61	3	$4PbO \cdot PbSO_4$
1.59	4	$4PbO \cdot PbSO_4$
1.58	3	$4PbO \cdot PbSO_4$
1.54	4	$4PbO \cdot PbSO_4$

On the other hand, these measurements prove also that the tribasic sulfate is not stable in this temperature range.

It can be established on the basis of thermal and classical analysis that in mass mixtures the total quantity of the sulfuric acid added has been used up for the formation of basic sulfate. Thus, on the basis of X-ray diffraction investigations, processes according to the following reaction schemes take place in mass mixing:

$$4PbO+H_2SO_4+nH_2O \rightarrow 3PbO \cdot PbSO_4 \cdot nH_2O+H_2O \qquad (3)$$

and in addition, both during aqueous and sulfuric acid mixing, one part of free Pb is oxidized:

$$2Pb+O_2 \rightarrow 2PbO \qquad (4)$$

X-ray diffraction analysis made possible the quantitative determination by thermal method and the determination of the composition of the mass. Calculation of the composition will be shown on the example of an experimental mass mixture. The following quantities of components were admixed. Naturally, PbO and Pb were added in the form of "lead dust", and one part of water as the component of sulfuric acid of 1.4 g ml^{-1} density.

Lead oxide (PbO)	59.3%
Free lead (Pb)	24.9%
Water (H_2O)	12.0%
Sulfuric acid (H_2SO_4)	3.8%
Total	100.0%

From the derivatogram recorded after mixing, the following can be established (see Fig. 1):

(a) at 100°C a decrease in weight of 10.3%, the loss of water;

(b) at 240°C a decrease in weight of 0.84%, the decomposition of $3PbO \cdot PbSO_4 \cdot nH_2O$;

(c) at 350°C an increase in weight of 0.84%, oxidation of free lead (Pb).

On the basis of the first step, the water content of the mass mixture is 10.3%.

The decomposition process in the second step on the basis of the X-ray diffraction measurements (see Table 3) can be written as follows:

$$3PbO \cdot PbSO_4 \cdot nH_2O+PbO \rightarrow 4PbO \cdot PbSO_4+nH_2O \qquad (5)$$

The determination of the composition of the tribasic sulfate and of the mixture makes necessary the determination or rather the calculation of "n". On the basis of the earlier assumptions, the total quantity of the sulfuric acid added has been used up for the formation of tribasic sulfate.

The quantity of tribasic sulfate can be simply calculated using eqn (3). It can be seen from the composition of the tribasic sulfate that "n" molecular weight of water belongs to a quantity of one molecular weight. To the quantity of basic sulfate, calculated on the basis of the sulfuric acid content, there belongs a quantity of water corresponding to the weight-loss in the second step. From this, the value of "n" can be calculated after reduction with the following simple equation:

$$n = \frac{\text{decrease in weight} \times 98}{\text{quantity of } H_2SO_4 \text{ added} \times 18}$$

The value of "n" obtained for the above mixture is 1.2. With a view to the deduction and basic assumption, this formula is valid only for a mass mixture, in which the quantity of sulfuric acid is on the basis of eqn (3) stoichiometrically equal to that of PbO, or less. If there is an excess of sulfuric acid, the above formula looses its validity. The limit is 25%, i.e., a mixture containing 1/4 part of sulfuric acid. However, this is only of theoretical importance, because mass mixtures suitable for battery manufacture contain considerably less sulfuric acid.

From the increase in weight in the third step of the derivatogram and of eqn (4), the quantity of Pb oxidized during mass mixing and that of PbO formed can be easily calculated. The PbO content of the mass mixture can be calculated by subtracting from the quantity of PbO added and formed during mixing, the quantity of PbO used up for the formation of the basic sulfate.

The result of the calculations for the composition of the mass is:

H_2O	10.3%
Pb	10.9%
$3PbO \cdot PbSO_4 \cdot nH_2O$	38.7%
PbO	39.7%
Total:	99.6%

It has been established in our investigations that the composition of the mass mixture can be determined by thermoanalysis with an accuracy of 1%.

Derivatographic and X-ray diffraction measurements carried out on the same mixture after 24 h of storage gave qualitatively identical results. However, the evaluation of the derivatogram (see Fig. 2) showed certain quantitative differences. With the proceeding of time, free lead still present has been completely oxidized, so that the step at 350 °C, indicating increase in weight, is missing on the derivatogram. Thus, the PbO content of the mass was further increased, while the $3PbO \cdot PbSO_4 \cdot nH_2O$ and H_2O contents relatively decreased in the composition.

The calculation of "n" from the measuring data gave interesting results. A values of 1.5 was obtained for "n", that is to say, it increased during storage. The conditions of storage were similar to those of the so-called aging operation, so that these results lead to a better understanding of the purpose of the aging process.

3.2 *Effect of the changing of the sulfuric acid content*

On the basis of a study of the literature and investigations carried out so far, it

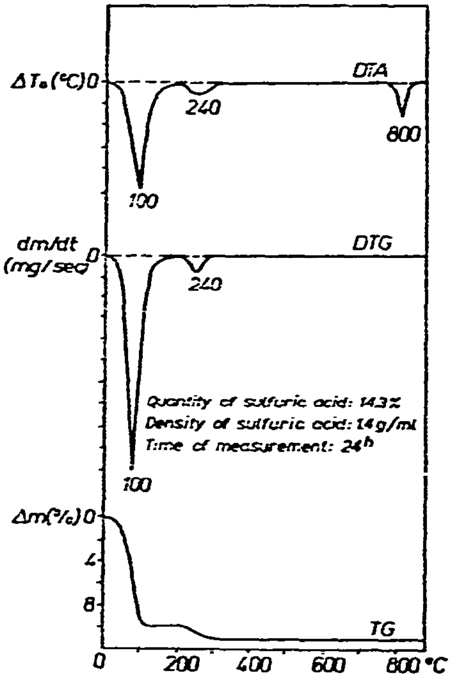


Fig. 2. Derivatogram of experimental mass mixture. Quantity of sulfuric acid: 14.3%; density of sulfuric acid: 1.4 g ml^{-1}; time of measurement: 24 h.

was thought expedient to investigate the effect of the change of the sulfuric acid content of the mass mixtures on the composition. An experimental series was prepared for the investigations, for practical purposes with the following quantities of sulfuric acid (the quantity of acid needed on the basis of the theoretical reaction (1) has been taken as 100%): 3.3, 8.3; 14.3; 25; 33.3; 50; 75; 100%. In the experimental series prepared in this way, the single mass mixtures contained 1–18 w/w % of sulfuric acid. The experimental series of eight members has been prepared with sulfuric acid of 1.4 g ml^{-1} density.

The mass mixtures prepared were subjected to thermal analysis immediately after their preparation (0 h) and after 24 h. The X-ray diffractograms of some of the mixtures were also taken. Calculating the composition of the single mass mixtures in the way described above, the following conclusions can be drawn from the derivatograms:

The composition of the mixtures is summarized in Table 4. An analysis of data in the table shows that the first four members of the series (3.3; 8.3; 14.3; 25%) consist of the same components. In these mixtures, PbO is in excess with respect to sulfuric acid on the basis of eqn (3). The quantity of basic sulfate increases proportionally with increasing sulfuric acid quantity. The character of the derivatograms is completely identical with that of the derivatogram of the 14.3% mixture described above (Fig. 1). X-ray diffraction measurements showed unequivocally for all the four mixtures the presence of $3PbO \cdot PbSO_4 \cdot nH_2O$ in addition to PbO and Pb.

TABLE 4

COMPOSITION OF THE MASS MIXTURES IMMEDIATELY AFTER MIXING

Density of sulfuric acid: 1.4 g ml^{-1}.

Compounds present	*Percentage composition*							
	Quantity of sulfuric acid (%)							
	3.3	*8.3*	*14.3*	*25.0*	*33.3*	*50.0*	*75.0*	*100.0*
H_2O	7.5	9.1	10.3	10.6	16.3	18.0	18.2	18.3
Pb	17.8	9.7	10.9	9.8	9.9	10.0	5.0	9.6
PbO	64.0	58.4	39.7	15.6	—	—	—	—
$3PbO \cdot PbSO_4 \cdot nH_2O$	9.0	22.4	38.7	62.2	73.6	26.1	—	—
$PbO \cdot PbSO_4$	—	—	—	—	—	45.6	72.0	58.2
$PbSO_4$	—	—	—	—	—	—	0.5	7.8
H_2SO_4	—	—	—	—	—	—	3.8	4.4
Total	98.3	99.6	99.6	98.2	99.8	99.7	99.5	98.3

A further study of the composition of the first four members of the experimental series shows that the composition of the mass mixtures (Table 5) did not change substantially after 24 h of storage. The free Pb content of the mass has further decreased, and accordingly, the quantity of PbO increased. Owing to the oxygen uptake of the mass, the quantity of basic sulfate has relatively decreased. Only the free lead content of the mixture with 14.3% sulfuric acid content, discussed above, has been completely oxidized during storage. Presumably, the composition and structure of this mass mixture provided the most favourable conditions for oxidation.

TABLE 5

COMPOSITION OF MASS MIXTURES 24 h AFTER MIXING

Density of sulfuric acid: 1.4 g ml^{-1}.

Compounds present	*Percentage composition*							
	Quantity of sulfuric acid (%)							
	3.3	*8.3*	*14.3*	*25.0*	*33.3*	*50.0*	*75.0*	*100.0*
H_2O	7.8	10.0	10.0	11.0	16.0	17.5	18.6	25.0
Pb	6.3	3.9	—	8.8	8.2	7.3	—	5.3
PbO	76.7	63.8	52.0	16.0	3.6	14.7	—	—
$3PbO \cdot PbSO_4 \cdot nH_2O$	8.9	22.1	37.7	63.4	62.6	—	—	—
$PbO \cdot PbSO_4$	—	—	—	—	9.2	60.2	71.5	25.0
$PbSO_4$	—	—	—	—	—	—	8.7	43.0
Total	99.7	99.8	99.7	99.2	99.6	99.7	98.8	98.3

A further analysis of the two tables shows that the composition of the second four experimental mixtures is less unambiguous (33.3; 50.0; 75; 100%), and changes also during storage. However, this can be easily understood, when the mixtures are more closely investigated on the basis of the facts established so far. According to eqn (3), it is in principle the 25% mixture, in which the quantities of PbO and H_2SO_4 are stoichiometrically equal. Nevertheless, the mixture contains unreacted PbO. This excess quantity is formed by the oxidation of the free Pb content of the mass mixture during mixing. Thus, the quantity of sulfuric acid, referred to the PbO content of the lead dust, is in practice lower than the percentage value used for the characterization of the mixture.

It can be seen from the table that due to oxidation, in the case of the 33.3% mixture the 4:1 ratio of lead oxide and sulfuric acid, i.e., the 25% mixture, has been exactly formed. It can be seen from the composition that the total quantity of PbO has been used up in the course of the chemical reaction. Thus, the basic sulfate content of this mixture is the highest. According to the X-ray diffractogram (see Table 6), here only the tribasic sulfate $3PbO \cdot PbSO_4 \cdot nH_2O$ is present.

TABLE 6

RESULTS OF THE X-RAY DIFFRACTION INVESTIGATIONS OF THE MASS

Quantity of sulfuric acid: 33.3%; density of sulfuric acid: 1.4 g ml^{-1}; time of measurement: 0 h.

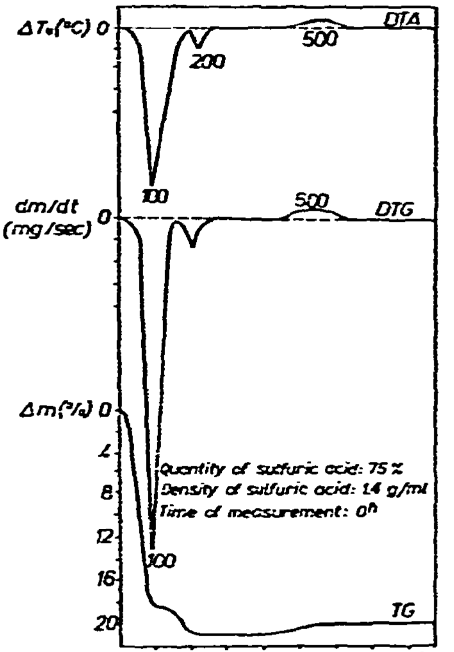
d_{hkl}	*Intensity*	*Cryst. phase*
9.8	3	$3PbO \cdot PbSO_4 \cdot nH_2O$
6.2	1	$3PbO \cdot PbSO_4 \cdot nH_2O$
5.7	2	$3PbO \cdot PbSO_4 \cdot nH_2O$
4.23	2	$3PbO \cdot PbSO_4 \cdot nH_2O$
3.60	2	$3PbO \cdot PbSO_4 \cdot nH_2O$
3.25	12	$3PbO \cdot PbSO_4 \cdot nH_2O$
3.13	12	$3PbO \cdot PbSO_4 \cdot nH_2O$
3.07	10	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.88	4	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.84	8	Pb
2.82	6	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.71	4	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.48	5	Pb
2.43	3	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.16	2	$3PbO \cdot PbSO_4 \cdot nH_2O$
2.08	2	$3PbO \cdot PbSO_4 \cdot nH_2O$
1.95	1	$3PbO \cdot PbSO_4 \cdot nH_2O$
1.86	4	$3PbO \cdot PbSO_4 \cdot nH_2O$
1.74	2	Pb
1.68	3	$3PbO \cdot PbSO_4 \cdot nH_2O$
1.63	2	$3PbO \cdot PbSO_4 \cdot nH_2O$

On the other hand, in the next mixture (50%) already actually the quantity of sulfuric acid is higher, as compared to PbO on the basis of eqn (3). In the presence of excess sulfuric acid, the quantity of the tribasic sulfate decreased considerably.

It can be established on the basis of the X-ray diffractogram that besides $3PbO \cdot PbSO_4 \cdot nH_2O$ the monobasic sulfate, $PbO \cdot PbSO_4$ appears. In the 50%

mixture, the tribasic sulfate is decomposed after 24 h, and is indicated also on the X-ray diagrams only in traces. The last four members of the experimental series are neither practically nor theoretically suitable for the manufacture of storage batteries, due on the one hand to their consistency (the quantity of water introduced increases also with increasing acid quantity of constant density), and on the other hand to their composition. Nevertheless these had also to be investigated, to obtain more complete conclusions.

This is particularly true for the last two members of the series, for the mixtures containing 75 and 100% of sulfuric acid, respectively. According to investigations on the derivatograph, performed immediately after the preparation of the 75% mixture (Fig. 3), the mixture cannot take up the total quantity of sulfuric acid, and the excess



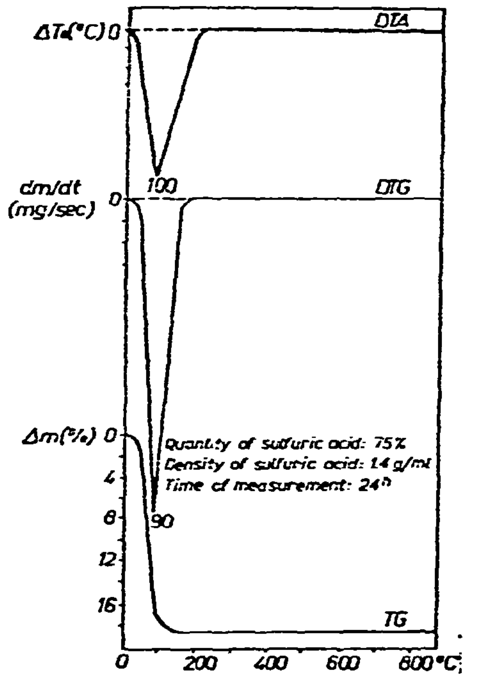


Fig. 3. Derivatogram of experimental mass mixture. Quantity of sulfuric acid: 75%; density of sulfuric acid: 1.4 g ml^{-1}; time of measurement: 0 h.

Fig. 4. Derivatogram of experimental mass mixture. Quantity of sulfuric acid: 75%; density of sulfuric acid: 1.4 g ml^{-1}; time of measurement; 24 h.

sulfuric acid was lost between 100 and 200°C. Predominantly the monobasic sulfate, $PbO \cdot PbSO_4$ has been formed in the mixture, but in traces $PbSO_4$ was already present. After 24 h of standing, sulfuric acid, first in excess, has been completely bound in the mixture (Fig. 4), and free Pb was further oxidized. According to X-ray diffraction investigations, here too $PbO \cdot PbSO_4$ represents the basic sulfate, but a small quantity of $PbSO_4$ is also present.

Neither in the preparation of the 100% mixture has the complete acid quantity been bound; according to the measurements performed this process is terminated only after 24 h. First $PbO \cdot PbSO_4$ and in smaller quantities $PbSO_4$ are formed in the mixture, and this composition shifts strongly during storage in the direction of $PbSO_4$.

We would like to mention in connection with the composition of the last two mixtures that the $PbO \cdot PbSO_4$ and $PbSO_4$ quantities in the table are not exact values, but this does not affect the conclusions drawn. The suspension-like consistency of the two mixtures limits strongly the homogeneity of the weighed-in samples, and thus, accurate determination. Within the series, the "*n*" values of the single mixtures containing tribasic sulfate have been compared (Table 7).

TABLE 7

CHANGE OF THE "*n*" VALUE OF TRIBASIC SULFATE AND OF ITS DECREASE IN WEIGHT, CHARACTERISTIC OF ITS QUANTITY, AS A FUNCTION OF THE QUANTITY OF SULFURIC ACID, MEASURED AT 0 AND 24 h

	Quantity of sulfuric acid (%)					
	3.3	*8.3*	*14.3*	*25.0*	*33.3*	*50.0*
"*n*" value at 0 h	0.5	1.1	1.2	0.9	0.45	0.1
"*n*" value at 24 h	0.6	1.3	1.5	1.0	0.55	0.0
Percentage decrease in weight, 0 h	0.1	0.45	0.85	1.0	0.5	0.13
Percentage decrease in weight, 24 h	0.1	0.5	1.0	1.2	0.6	—

The "*n*" value first increases with increasing quantity of sulfuric acid, passes through a maximum, and then decreases. This is clearly shown also by Fig. 5.

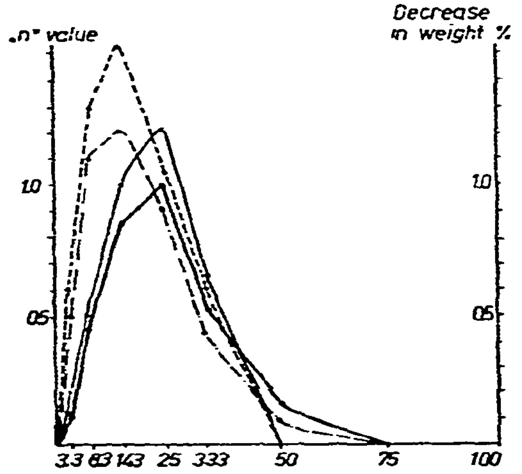


Fig. 5. Change in "*n*" value and percentage decrease in weight as a function of the quantity of sulfuric acid in mixtures prepared with sulfuric acid of 1.4 g ml^{-1} density. —·—·—, "*n*" 0 h; — — — —, "*n*" 24 h; ————, % decrease in weight, 0 h; ————, % decrease in weight, 24 h.

The quantity of the basic sulfate changes in a similar way. The change in the quantity of the basic sulfate has also been plotted in the figure, but instead of the percentage values used for the characterization of the composition, where the quantitative shift of other components would interfere, the percentage values of the decrease in weight occurring during the decomposition of the tribasic sulfate have been plotted as a function of the quantity of sulfuric acid, referred to PbO. However, the maxima of the two curves do not coincide. The maximum of the "*n*" value belongs to the 14.3% composition, while that of the quantity of the basic sulfate to the 25% composition.

In addition to the determination of the presence and the unique role of tribasic sulfate with water content ($3PbO \cdot PbSO_4 \cdot nH_2O$) in the mass and to the determination of the composition of mass mixtures, this is the third most important result of our experimental work on mass mixtures. The fact that preferential compositions exist, is of great importance from the point of view of the quantity of sulfuric acid to be used in the formulations. However, in the selection of the most ideal mass mixture, mass mixing cannot be discussed detached from the production line. For example, it is essential to take into consideration also the development of a composition, which ensures the most favourable change in gram molecule volume during formulation.

In the mass mixtures, the value of "*n*" increases during storage, and tribasic sulfate is stabilized under minimum water uptake. This increase occurs in each mixture as can be seen also from Fig. 5.

The water content of the basic sulfate is only of the order of 1 w/w%, but under consideration of the ratios of the molecular weights, it can be easily understood that it has a considerable effect on the structure and the properties of mass mixtures.

3.3 Effect of the change in density of sulfuric acid

The effect of the change in density of sulfuric acid on the composition of the mass mixture has also been investigated in the course of our experiments.

The following mixtures were prepared:

mixing with sulfuric acid of a density of 1.1 g ml^{-1}; in this mixture no water has been introduced;

premixing with sulfuric acid of a density of 1.1 g ml^{-1}, followed by mixing with sulfuric acid of 1.4 g ml^{-1} density;

mixing with sulfuric acid of 1.4 g ml^{-1} density, aqueous pre-mixing;

mixing with sulfuric acid of 1.6 g ml^{-1} density, aqueous pre-mixing.

According to the above, mixtures were prepared for the investigations with both 8.3 and 14.3% quantities of sulfuric acid, used in practice.

The investigations were carried out immediately after mixing, and 24 h later. An evaluation of the measurements shows that the total quantity of sulfuric acid added has been bound in each mass mixture. Here too, one part of free Pb has been oxidized during mixing, and the quantity of free Pb changed only slightly during storage. The water content of the basic sulfate was found to be lower in the 1.1 g ml^{-1} and 1.6 g ml^{-1} mixtures, than in the case of the 1.4 g ml^{-1} mixtures.

The behaviour of the "*n*" values calculated from this for the various mixtures is interesting (see Table 8). The value of "*n*" was highest for mixtures prepared with sulfuric acid of 1.4 g ml^{-1} density, most often used in practice, and within these for the mixture of 14.3%. According to practical experiences, the density of 1.4 g ml^{-1} is the best, which is linked again in the experiments to a preferential maximum value. After 24 h of storage, "*n*" values generally increased, but, with the exception of the 1.4 g ml^{-1} and the 1.1+1.4 g ml^{-1} mixtures, only by a rather minimal value. In the case of masses mixed with 1.6 g ml^{-1} sulfuric acid, a deviation from experiences gained so far was met, because here the "*n*" value of the mass mixed with a quantity of 8.3% and was higher than that of the 14.3% mixture. This difference was equalized at the end of 24 h of storage.

TABLE 8

CHANGE OF THE "*n*" VALUE OF TRIBASIC SULFATE AS A FUNCTION OF THE DENSITY AND OF THE QUANTITY OF SULFURIC ACID, MEASURED AT 0 AND 24 h

Quantity of sulfuric acid (%)	*Time of measurement (h)*	*Density of sulfuric acid (g ml^{-1})*			
		1.1	*1.1+1.4*	*1.4*	*1.6*
8.3	0	0.8	0.8	1.1	0.8
14.3	0	1.0	0.9	1.2	0.5
8.3	24	1.0	1.2	1.5	0.85
14.3	24	1.0	1.3	1.5	0.85

DISCUSSION

The experiments proved that thermoanalytical investigations can be used for the investigation and control of the processes of storage battery manufacture, and for the determination of the composition of products, produced in the single phases. This has been proved for both industrial and experimental manufacture.

The cardinal point in the manufacture of battery plates is the chemical process proceeding in mass mixing, and the composition of the mass prepared. It has been proved in the course of the experiments by thermoanalytical and X-ray diffraction investigations that not with standing contradictory data in the literature, tribasic sulfate of the composition $3PbO \cdot PbSO_4 \cdot nH_2O$ is formed in mass mixing. This determines also the chemical process proceeding in practice.

It has been established in the course of laboratory investigations that on increasing the sulfuric acid content of the mass, first both the tribasic sulfate content of the mass and the "*n*" value of the basic sulfate increase, and after passing through a maximum value, both decrease rapidly. According to our investigations, the two maxima do not coincide. Tribasic sulfate is formed in maximum quantity, when 25% of the sulfuric acid quantity, referred according to equation $PbO+H_2SO_4 \rightarrow PbSO_4+H_2O$ on the total PbO content of the mass (PbO formed during mixing included), is admixed. The maximum of the "n" value of $3\mathrm{PbO}\cdot\mathrm{PbSO_4}\cdot n\mathrm{H_2O}$ is obtained on admixing a quantity of 14.3% of sulfuric acid.

The density of sulfuric acid used for mass mixing has also an important effect. Experiments performed with sulfuric acid of various densities proved that the basic sulfate content of the mass depends also on the density of sulfuric acid. With increasing density, the basic sulfate content and the value of "n" first increase, then decrease. The maximum value is obtained when sulfuric acid of 1.4 g ml^{-1} density is used.

The importance of the role of $3\mathrm{PbO}\cdot\mathrm{PbSO_4}\cdot n\mathrm{H_2O}$ and the value of the experiments are supported by the fact that practical experiences of many decades have established for the composition of mass mixtures a quantity of 14.3% sulfuric acid, which is near the maximum of "n", and that the density of sulfuric acid most often used in practice is 1.4 g ml^{-1}. Thus empirical knowledge has been complemented by the present work, and some theoretical problems have been solved.

In the course of the experiments carried out so far, only the positive electrode of motor car starting batteries has been investigated[34,35]. However, the results of the conclusions drawn are pertinent also to the manufacture of acid batteries of other types, and it is thought even that they can be extended to a certain measure to the manufacture of the negative electrode.

REFERENCES

1 G. Vinal, *Storage Batteries*, New York, 1955.
2 J. P. Moll, *Die Fabrikation von Bleiakkumulatoren*, Leipzig 1952.
3 C. Drotschmann, *Bleiakkumulatoren*, Weinheim, 1951.
4 L. Pesty, *Akkumulátorok, Elemek* (*Storage Batteries, Cells*), Müszaki Könyvkiadó, Budapest, 1962.
5 G. Bazalgette, *Batterien*, 14 (1960) 6.
6 C. Drotschmann, *Batterien*, 16 (1962) 317.
7 Toelle and von Hofe: *DRP*, 186, 972 (1905) and 187, 946 (1905).
8 T. Takagaki, *Batterien*, 17 (1963) 553.
9 J. Burbank, *J. Electrochem. Soc.*, 113 (1966) 10.
10 J. N. Mrgudich, *Trans. Electrochem. Soc.*, 81 (1942) 165.
11 J. J. Lander, *Naval Research Lab. Rept. C-3262*, 1948.
12 A. C. Simon, *Batterien*, 18 (1964) 690.
13 D. A. Mac Innes, *Am. Electrochem. Soc. Chem. Met. Eng.*, 22 (1920) 727.
14 F. A. Schneider, *Batterien*, 14 (1960) 64.
15 J. W. Meilor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 7, London, 1930, p. 565.
16 Gmelin-Krauts, *Handbuch der anorganischen Chemie*, Vol. 4, Heidelberg, 1924, p. 225.
17 R. H. Greeburg, F. B. Finan and B. Angruss, *J. Electrochem. Soc.*, 98 (1951) 474.
18 *U.S. Pat.* 3.194.695 (1964/1965); *Batterien*, 20 (1966) 910.
19 C. Drotschamnn, *Batterien*, 19 (1965) 761.
20 DAS 1.173.154/21b (1960) 64; Varta, *Batterien*, 19 (1966) 848.
21 E. Woss and J. Freundliche, *Batterien*, 20 (1966) 909.
22 *U.S. Pat.* 3.173.810 (1965); *Batterien*, 20 (1966) 943.
23 *French Pat.* 1.383.278 (1963/1964); *Batterien*, 19 (1966) 848.
24 T. Takagaki, *Angew. Chem.*, 73 (1961) 116.
25 H. C. Hofman and W. Wanjukow, *Bull. Am. Inst. Min. Eng.*, (1912) 889.
26 H. M. Kellogg and S. K. Basu, *Trans. Met. Soc. AIME*, 218 (1960) 70.
27 J. J. Lander, *J. Trans. Electrochem. Soc.*, 95 (1949) 174.

28 J. D. Esdaile, *J. Electrochem. Soc.*, 113 (1966) 71.
29 R. Schenk and W. Rassbach, *Ber. Z. Chem. Gesell.*, 41 (1908) 2917.
30 F. M. Jager and H. C. Germs, *Z. Anorg. Chem.*, 119 (1921) 145.
31 G. Tridot, J. C. Bonin and D. Thomas, *J. Therm. Anal.*, 1 (1969) 35.
32 F. Paulik, J. Paulik and L. Erdey, *Z. Anal. Chem.*, 160 (1958) 241.
33 G. Liptay, M. Berényi and E. Sárkány, *Hung. Sci. Instr.*, 15 (1968) 31.
34 L. Sors and G. Liptay, *4th ICTA, Budapest, 1974, Therm. Anal.*, 3 (1974) 657.
35 L. Sors, I. Porubszky and G. Liptay, *Hung. Sci. Instr.*, 28 (1973) 31.