

## THE EFFECT OF ADDITIVES ON THE POSITIVE LEAD-ACID BATTERY ELECTRODE\*

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### Summary

The effect of the additives carboxymethylcellulose (CMC), carbon black, silica gel, and fibres on the manufacture of positive active material and on the cycle life was investigated by means of porosimetry, inner surface (BET) determination, X-ray diffractometry, chemical analysis, and by measuring the course of the potential, by testing the low rate and high rate capacities and by overcharge cycling tests

It was shown that the additives can be classified, according to their mode of action, into additives

- (a) increasing the water accumulating capacity of the paste,
- (b) influencing the crystallization of the mass,
- (c) increasing the electronic conductivity of the mass,
- (d) stabilizing the mass

Types (a), (b), and (c) affect the manufacture of active material and the initial capacities, whereas additive (d) improves the cycle life

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### 1. Introduction

The specific capacity of the positive lead-acid battery electrode can be increased by increasing the utilization of the active mass. This can be achieved by changing the manufacturing conditions of the active material. In respect of production-technological requirements, to a first approximation this method resulted in an optimum, which could be explained on the basis of an extensive systematic investigation. On the other hand, improvements were also achieved using additives, especially in the active mass, however, their mode of action has not yet been fully explained. First considerations were made by Dasoyan *et al* [1] as well as by Reinhardt *et al* [2].

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\*Dedicated to Prof. Dr. Ernest Yeager of Case Western Reserve University, Cleveland, U.S.A. on the occasion of his 60th birthday and in appreciation of his scientific merits.

Ideas on the use of promising additives are given in references (*e g* , 3, 4, 5, 6). This paper tries therefore to provide information on the principal effects, including the mode of operation, and on the starting point and duration of efficiency of such additives

## 2. Experimental

Carbon black (acetylene black P1250), silica gel (particle size 30 - 150 nm), carboxymethylcellulose (CMC), and fibres (Dynel floc) were used as additives

Investigations were mainly carried out on 3 A h electrodes. In addition, 15 A h electrodes were used for capacity tests

To prepare the paste, 1 kg of dry lead dust (ball mill, approx 20% Pb, 80% tet PbO), with or without the corresponding additives, was dry mixed, then wet mixed with 133 ml of H<sub>2</sub>O for 10 min. 71 ml of H<sub>2</sub>SO<sub>4</sub> (density,  $\rho = 1.4 \text{ g/cm}^3$ ) were then added over a period of 25 min and mixing was then continued for an additional 5 min

After mixing, the consistency of the paste was measured. This was achieved by using the simple method of the penetration of a graduated conical measuring body into the paste.

Curing was carried out at a relative humidity of 95% and at a temperature of 23 °C for 10 days. Subsequently the electrodes were dried at 60 °C for one hour

After soaking in acid for one hour, formation took place in H<sub>2</sub>SO<sub>4</sub> of density 1.05 g/cm<sup>3</sup> and at a temperature of 25 °C. It was carried out for 40 h at a current density of 6 mA/cm<sup>2</sup> and afterwards for an additional 6 h at 4 mA/cm<sup>2</sup>. The formed electrodes were then washed acid-free and oven-dried at 80 °C for 15 h

To determine the phase composition of cured and formed masses, the Co K $\alpha$  line of the TuR-M 61 X-ray diffractometer (Dresden, GDR) was used. The pore volume and the pore size distribution were measured with a Carlo-Erba porosimeter (Series 200), and the BET-surface was determined using a Carlo-Erba sorptomatic apparatus (Series 1800). The analytical and measured data were obtained, respectively, by averaging at least two samples of electrode material and two electrodes

The low rate and high rate capacity tests were carried out at currents of

$$I \hat{=} \frac{1}{20} \left( \frac{C_{\text{th}}}{2} \right) \text{ A} \quad \text{and} \quad 3 \left( \frac{C_{\text{th}}}{2} \right) \text{ A}$$

respectively, where  $C_{\text{th}}$  is the theoretical capacity

The cycle life was investigated by a standard national test regime (TGL 10241). Sets of one positive electrode and two negative electrodes were alternately discharged and charged at a current  $I \hat{=} \frac{1}{10} (C_{\text{th}}/2) \text{ A}$  for 1 h and 5 h, respectively. After 36 cycles, and following an open circuit stand of 96 h, the low rate and high rate tests were undertaken. The test points are averaged

values of five measurements for the high rate tests and three measurements for the low rate tests.

### 3. Results and discussion

#### 3.1 Influence of the additives during the manufacture of active material

##### 3.1.1 Paste preparation

The cured electrode structure is particularly determined by the quantities of sulphuric acid and water accumulated during the paste preparation. A porosity increase, which is aimed for in most cases, cannot be achieved by an extreme increase in the paste water content alone, mainly for reasons of paste workability [7]. As shown in Fig. 1, however, pastability can be influenced by additives. Decreasing penetration depth indicates that the water absorption of the paste\* is increased mainly by the addition of CMC, but to some extent, also by carbon black. Consequently, additional water absorption without deterioration of the paste workability is possible, espe-

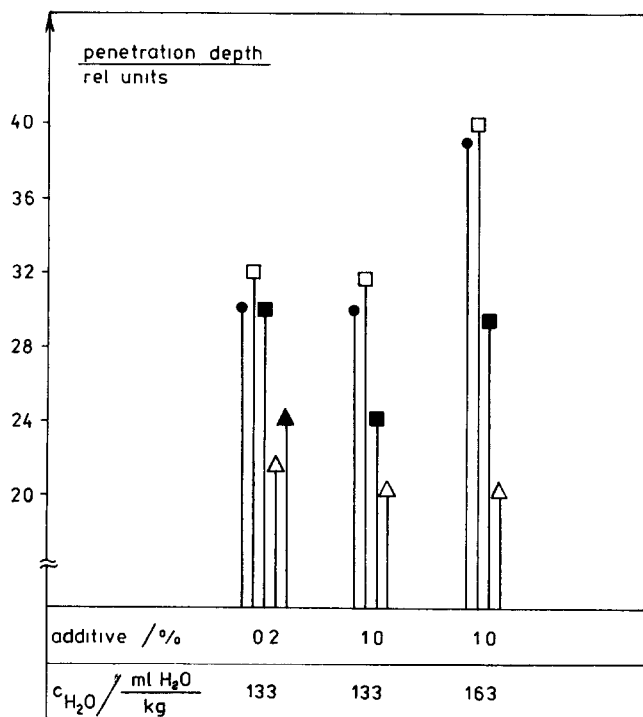


Fig 1 Paste penetration, after mixing, as a function of water content and additive concentration. Additive ●, none, □, silica gel, ■, carbon black, △, CMC, ▲, fibre

\*The unexpectedly low penetration of the fibre formulation can be explained, primarily, as being due to the elasticity of the fibres

cially in the case of CMC-containing masses The effect of CMC addition is assumed to be due to its known swelling and dispersion-stabilizing properties [8]

3 1 2 Curing

The influence of additives on the processes taking place in the paste during curing, i.e.,

- (a) oxidation of the residual free lead,
- (b) drying
- (c) formation of basic lead sulphates,

was studied by (a) the chemical analytical determination of the concentration of free lead, (b) the gravimetric determination of the water content of the paste in dependence on the curing time (Fig 2), and (c) by X-ray diffraction patterns

Figure 2 indicates that CMC and carbon black additives contribute to an accelerated oxidation of free lead and to an improvement in the curing effect (lower lead content)

This result is not easily understood The oxidation of free lead by oxygen in the presence of water, however, may be regarded as the reaction of a short-circuited galvanic cell (eqn (3)) with the following anodic (eqn (1)) and cathodic (eqn (2)) partial processes

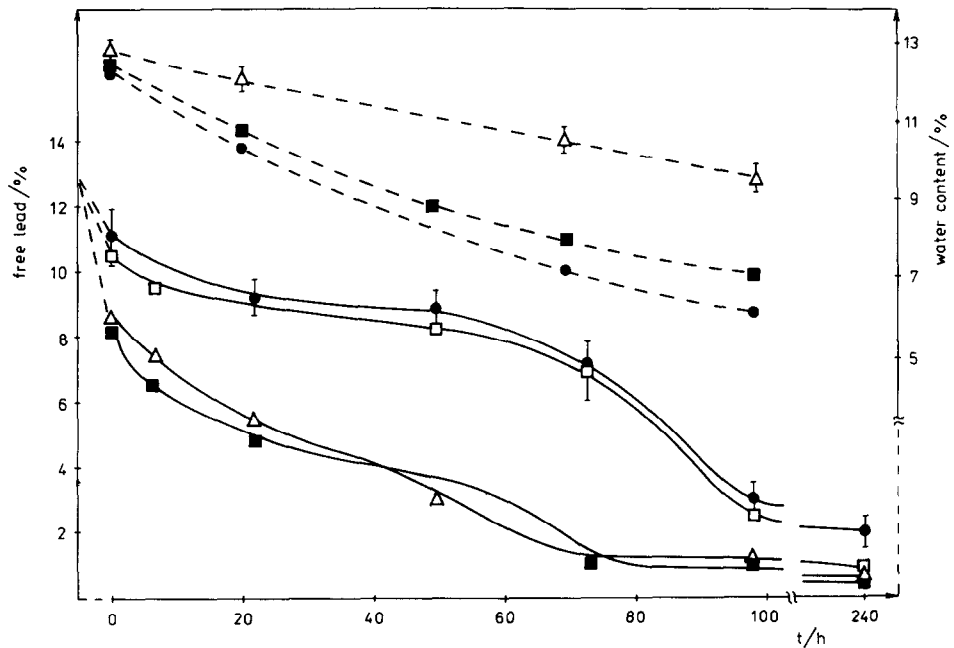


Fig 2 Changes in the water and free lead contents of pastes with additives (1 0%) as a function of the curing time Free lead, —, water content, - - - Additive ●, none, □, silica gel, ■, carbon black, △, CMC, ▲, fibre

TABLE 1

Pore volume ( $V$ ) in the range of fine and coarse pores, and specific surface ( $A$ ) of cured masses with additives

Additive Type	Concentration (%)	$V$ ( $10^{-3} \text{ cm}^3 \text{ g}^{-1}$ )		$A$ ( $\text{m}^2 \text{ g}^{-1}$ )
		Pore range		
		$r_p$ 4 - $10^2$ nm	$r_p$ $10^2$ - $2 \times 10^3$ nm	
None	—	9	77	1.5
Silica gel	0.2	16	68	1.8
Fibre	0.2	13	83	1.5
CMC	0.2	42	52	2.2
	1.0	40	59	2.2
Carbon black	0.2	12	95	1.3
Absolute error $\pm$		2	3	0.1



This would be analogous to the oxidation of cadmium in the overcharge of gas proof nickel-cadmium accumulators [9]. No doubt the oxidation kinetics of the free lead will also be determined by the oxygen reduction (eqn. (2)).

Decrease of the oxygen overvoltage can be achieved by

— the application of catalysts for oxygen reduction

— the formation of a large surface area contact between Pb, H<sub>2</sub>O, and

O<sub>2</sub>

It is assumed that, as usual (see also ref. 10), carbon black acts as a catalyst and that CMC provides a large surface area contact for an extended period of time. The latter assumption is based on

— the dispersion effect of the additive and the homogeneous distribution of the water, which is smeared like a gel over the paste, thus resulting in the formation of thin water films on the increased pore surface (see Table 1),

— the preservation of these "catalytically acting" water films [7] by reducing water depletion of CMC-containing pastes (Fig. 2)

Thus, with CMC, the optimum humidity range of 3-8% [11] for curing could be extended

The proportions of the single lead phases after curing are not influenced by additives [12] under the given experimental conditions

Table 1 presents the secondary structure of cured pastes. In general, it can be seen that, mainly due to the increase in the water absorption of the paste, the porosity is increased by the addition of carbon black, and also by CMC and fibres.

Whereas an increase in pore volume resulting from the presence of larger pores is apparent in carbon black formulations, additional fine pores are formed when CMC is used. This is also reflected in the BET surface area. In addition, the percentage of smaller pores is increased at the expense of larger pores in CMC formulations due to the dispersion effect of CMC and retardation of water removal.

### 3.1.3 Phase formation

During formation, the electrochemical oxidation of the PbO components of the mass into  $\alpha$ -PbO<sub>2</sub> takes place initially, and subsequently PbSO<sub>4</sub> is converted into  $\beta$ -PbO<sub>2</sub> [13, 14].

The ratio of the two reactions in the total conversion of the formation is reflected in the course of the formation potential (under load), as well as in the change of the electrode composition. The course of formation is influenced by changing pH-value-dependent kinetic hindrances of the transport processes and, in addition, mainly by the surface area change of the PbO/ $\alpha$ -PbO<sub>2</sub> contact.

At the beginning of formation, this surface area contact, located initially in the vicinity of the grid, grows, due to the increasing formation of  $\alpha$ -PbO<sub>2</sub> and the increasing electronic conductivity. As a result the polarizations are reduced and the formation potential decreases (Fig. 3).

With increasing formation time, however, due to chemical sulphation and consumption of PbO components, the surface area of PbO/ $\alpha$ -PbO<sub>2</sub> contact decreases. This finally results in an increase (slope) in the formation potential. According to Pavlov *et al.* [13], this slope is due to the change of the potential-determining process, i.e., the beginning of the  $\beta$ -PbO<sub>2</sub> formation from PbSO<sub>4</sub>.

Since sulphation depends on the pore structure and on the local pH value, additives may influence the course of formation or the PbO/ $\alpha$ -PbO<sub>2</sub> surface area contact by a change not only of the electronic conductivity, but also of the electrode structure.

Therefore, due to the fine-grained structure of CMC-containing masses (Table 1) and the fast pore acidification, a considerable and rapid PbSO<sub>4</sub> formation (Fig. 4) occurs leading to high electrochemical polarizations (see Fig. 3). The potential slope is consequently forced up (Fig. 3) and the  $\alpha$ -PbO<sub>2</sub> formation is limited (Fig. 4). The preferred  $\beta$ -PbO<sub>2</sub> formation can also be explained by the fine pore structure which hinders the transport away of H<sub>2</sub>SO<sub>4</sub>.

Conversely, the decrease in the level of the formation potential and retardation of the potential slope by the addition of carbon black (Fig. 3),

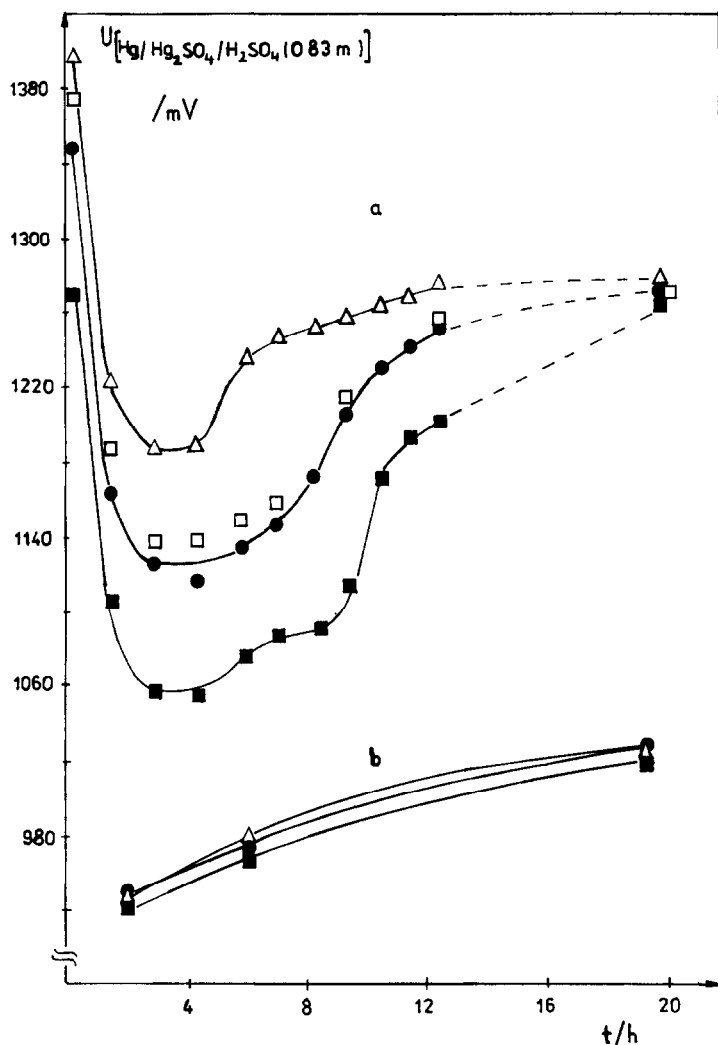


Fig 3 (a) Formation potential and (b) open circuit potential of different cured masses with additives (1.0%) as a function of formation time ( $i \approx 16 \text{ A/kg} \approx 6 \text{ mA/cm}^2$ ) Additive  $\bullet$ , none,  $\square$ , silica gel,  $\blacksquare$ , carbon black,  $\triangle$ , CMC

indicate a long term  $\alpha\text{-PbO}_2$  formation (see also Fig 4). This is only partly caused by the coarse porous mass of the carbon black formulation. It is a result, mainly, of the increased electronic conductivity of the carbon black-containing mass and the extension of the  $\text{PbO}/\alpha\text{-PbO}_2$  surface area contact at the beginning of formation. When using carbon black-free formulations, the  $\text{PbO}_2$  zone originating during formation is closely spaced and located near the grid. This can be explained by the almost exclusively ionic charge transport. On the other hand, due to the intrinsic conductivity of added carbon black [12, 16], electrically conductive strings can be formed in the

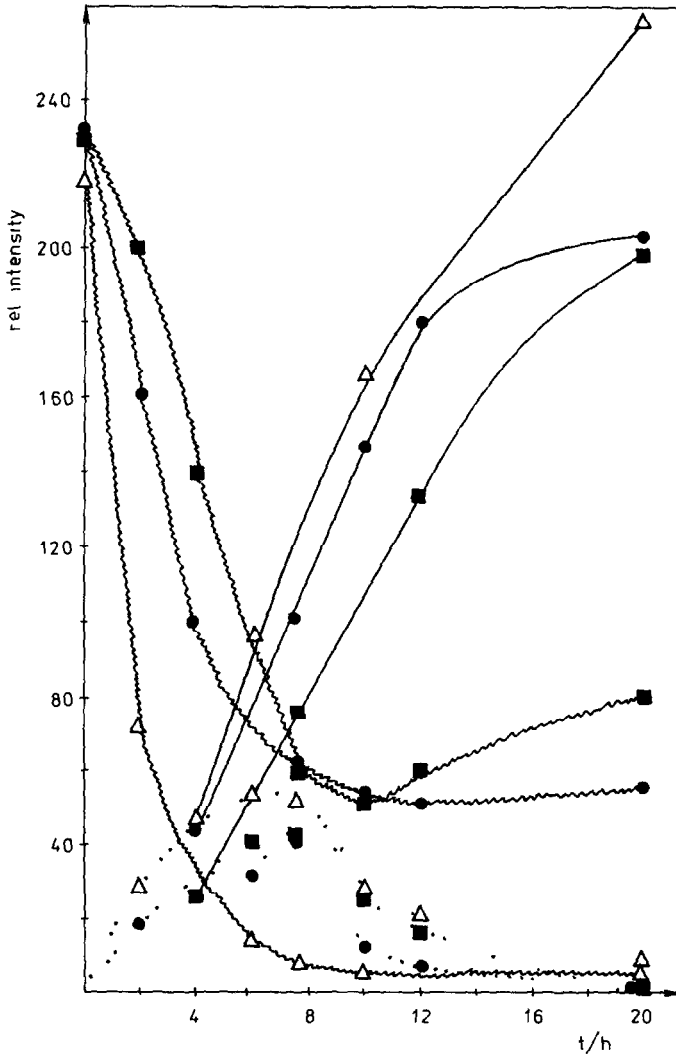


Fig 4 Relative intensities of the following phases as functions of the formation time and the type of additive in the formulation  $d = 300$  pm ( $\text{PbSO}_4$ ),  $d = 312$  pm (tet  $\text{PbO} + \alpha\text{-PbO}_2$ ) characteristic for  $\alpha\text{-PbO}_2$  after 12 h,  $d = 350$  pm ( $\beta\text{-PbO}_2$  only)  $\text{PbSO}_4$  line ( $J = 33$ ) [15] eliminated Additive (1 0%)  $\bullet$ , none,  $\blacksquare$ , carbon black,  $\triangle$ , CMC

cured mass which also participate in the charge transport. Consequently, not only the electrochemical polarizations, but also the ohmic potential drop, are decreased.

Whereas formed electrodes with CMC and carbon black thus have, respectively, a lower or a higher ratio of  $\alpha\text{-PbO}_2$  to  $\beta\text{-PbO}_2$  (Figs 4, 7), silica gel and fibre additives do not influence the course of the potential and the primary structure.



TABLE 2

Pore volume ( $V$ ) in the range of fine and coarse pores, and specific surface ( $A$ ) of active masses with additives after formation

Additive		$V$ ( $10^{-3} \text{ cm}^3 \text{ g}^{-1}$ )		$A$ ( $\text{m}^2 \text{ g}^{-1}$ )
Type	Concentration (%)	Range of pores		
		$r_p$ $4 \cdot 10^2 \text{ nm}$	$r_p$ $10^2 \cdot 2 \times 10^3 \text{ nm}$	
None	—	13	81	3.9
Silica gel	0.2	16	84	4.1
Fibre	0.2	11	92	4.1
	1.0	16	75	4.0
CMC	0.2	17	83	4.5
	1.0	22	77	4.6
Carbon black	0.2	14	85	3.9
	1.0	16	86	4.0
Absolute error $\pm$		1.5	3	0.15

The secondary structures of the formed electrodes are shown in Table 2, from which it is obvious that

- all additives contribute to a relative increase in porosity,
- with CMC formulations and, to a lesser degree, with silica gel formulations, the fine-grained structure developed in the course of curing is preserved;

- increase of the CMC content leads to a finer-grained structure of the formed electrode which is not due to any additional water absorption by the paste (*cf* Tables 1, 2) or to a further change in the  $\alpha/\beta\text{-PbO}_2$  ratio [12].

The latter result indicates that CMC has a concentration-dependent protective colloid effect (inhibition of crystal growth)

### 3.1.4 Electrical performance

The initial values of the electrical performance of the lead dioxide electrodes indicate the positive influence of 0.2% CMC and silica gel, which is shown as a 5% and 10% improvement in the low rate and the high rate capacities, respectively (Table 3). Carbon black and fibres do not show any appreciable influence. This can be explained as follows

Electrodes with 0.1–0.2% CMC are characterized by an increased porosity and a fine grained structure (Tables 1, 2), which is caused by the high water absorption capacity of the paste with CMC, and by the slow escape of water from the paste, the protective colloid effect of CMC and the high  $\beta\text{-PbO}_2$  content, respectively. These result in good initial electrical values.

TABLE 3

Mass-related initial capacities of electrodes with additives after formation (the average error of the mean value,  $\Delta\bar{s}$ , at 25 °C is given)

Amount of additive (%)	Type of additive	Low rate capacity (% $C_{th}/2$ )	$\Delta\bar{s}$ (% $C_{th}/2$ )	High rate capacity (% $C_{th}/2$ )	$\Delta\bar{s}$ (% $C_{th}/2$ )
—	None	113 0	1 7	33 3	1 2
0 2	CMC	118 1	1 6	36 6	0 6
0 2	Silica gel	117 0	1 3	37 2	0 9
0 2	Carbon black	116 0	1 0	32 5	0 8
0 2	Fibres	114 1	1 8	33 7	1 2
—	None	113 0	1 7	33 3	1 2
1 0	CMC	114 5	1 6	34 5	1 2
1 0	Silica gel	114 0	1 6	30 8	1 7
1 0	Carbon black	114 5	2 9	33 7	1 8
1 0	Fibres	110 0	3 0	—	—

Electrodes with a low concentration of carbon black (0.2%) show an increase in porosity which is not caused by the intrinsic porosity of the additive. On the other hand, the active mass is coarsely-grained (Table 2), mainly due to the high  $\alpha$ - $PbO_2$  content. Consequently, the initial electrical values are not improved significantly (see also ref. 17).

The increase in the electrical performance in the presence of 0.2% silica gel is difficult to interpret, since no pronounced changes of physico-chemical structural parameters occur. It seems therefore that silica gel can act as a foreign seed, favouring nucleation and leading to an increase of fine pores (Table 2). The good high-rate capacity, however, suggests an additional effect. Thus, silica gel could serve as an acid storage reservoir at high rates of discharge.

The structure of the active mass is hardly influenced by fibres. As shown by micrographs [12], however, low quantities of fibres (0.2%) lead to the formation of additional cavities between the active mass and the additive (Table 2) which act as ionically conductive paths [12]. The electrical performance, however, is not improved, since the fibres prevent a uniform discharge due to their size and insulating properties. The increase in the additive concentration from 0.2% to 1.0% has a negative effect throughout. This is especially due to

— inhomogeneities in the electrode structure caused by the presence of the additives (fibres) and by the oxidation of additives (CMC, carbon black [12]);

— a decrease in the porosity, as well as structural and transport restrictions during discharge, if the pore structure becomes too fine as a result of the addition of CMC (Table 2),

— a decrease in the ionic conductivity due to blocking of the diffusion paths by additives (fibres, silica gel [12]).

### 3.2 Influence of additives during cycling

Continuous charge and discharge cycling is taken as the standard to assess the operational life of electrodes. As control investigations have shown, differences in the cycle life under the cycling conditions used in this work result only from the structural properties of the active masses (Figs 5, 6).

Whereas at the beginning of cycling, due to an improved subsequent formation, the initial values are also improved, with progressive sludging of the mass (from about the 144th cycle) a reduction in the electrical performance occurs. In regard to the influence of the additive, the following conclusions can be drawn

— The operational life (Figs 5, 6) is increased only by fibre addition due to the mechanical stabilization of the active mass. Also involved is a structure-preserving influence [6], which is indicated by a relatively smaller decrease of the  $\alpha/\beta$ - $\text{PbO}_2$  ratio (Fig 7)

— Silica gel does not have a negative influence on the cycle life. According to ref. 5, an active-mass-stabilizing influence is even ascribed to the addi-

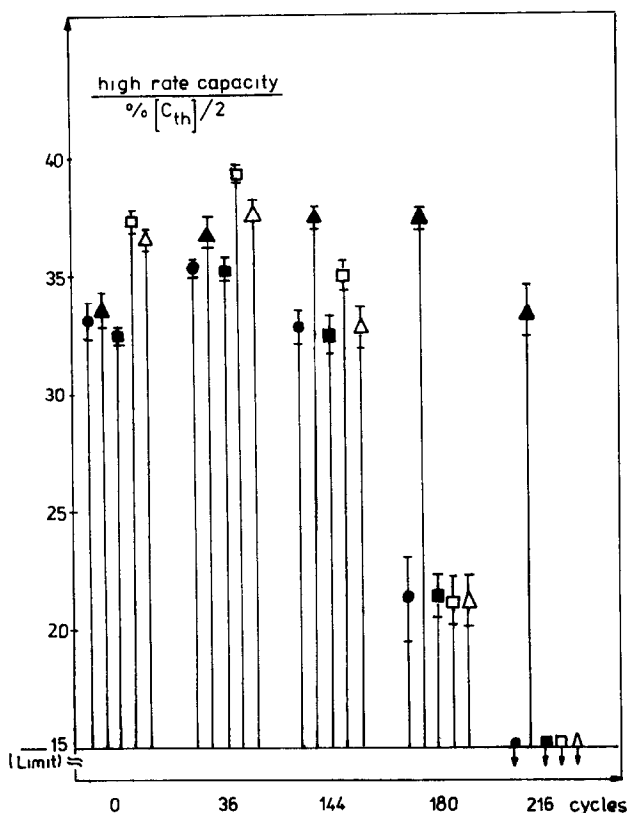


Fig 5 Changes in the high rate capacity of active masses with additives (0.2%) during cycling. Additive: ●, none; □, silica gel; ■, carbon black; △, CMC; ▲, fibre

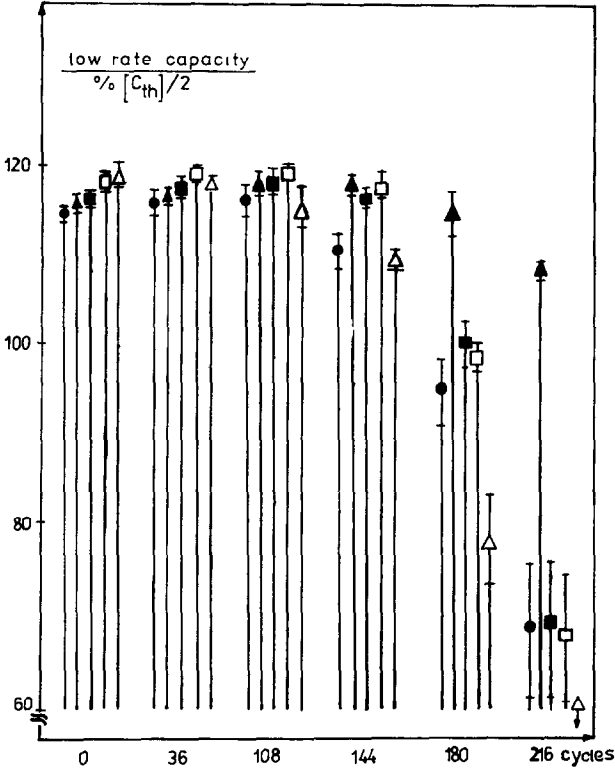


Fig 6 Changes in the low rate capacity of active masses with additives (0.2%) during cycling. Additive ●, none, □, silica gel, ■, carbon black, △, CMC, ▲, fibre

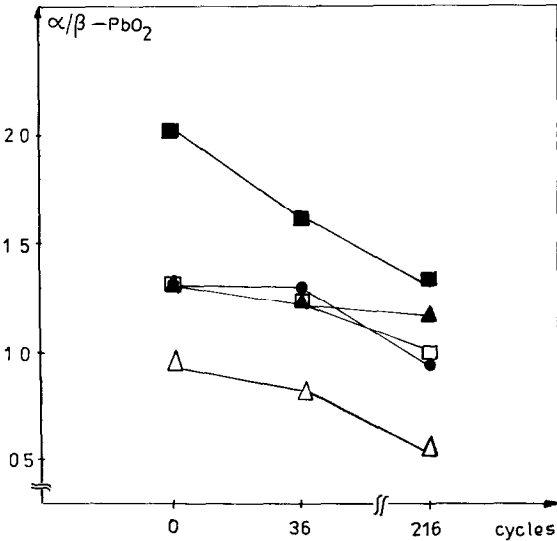


Fig 7 Change in the ratio of  $\alpha\text{-PbO}_2$  to  $\beta\text{-PbO}_2$  of active masses with additives (0.2%) during cycling. Additive ●, none, □, silica gel, ■, carbon black, △, CMC, ▲, fibre

tive, this influence being attributed to the interaction of silica gel OH groups with  $\text{PbO}_2$ -hydrating water

— The addition of CMC leads to a rapid mechanical destabilization of the active mass structure [18] due to the decrease of an initially low  $\alpha/\beta\text{-PbO}_2$  ratio (Fig 7) and the removal of this additive by oxidation during overcharge. This leads to an early mass sludging and a decrease in the cycle life (Fig 6)

— When using carbon black, the negative structural effect caused by the oxidation of this additive [12] is compensated for by the influence of the high  $\alpha\text{-PbO}_2$  content, which is also highest at the end of cycling (Fig. 7).

#### 4. Conclusions

The addition, to the positive mass of the lead-acid accumulator, of additives can influence the primary and secondary structures in a purpose-oriented way. This results in an improvement of the electrical performance.

Under the given conditions of manufacture it is obvious that

— fine-grained active masses with a large specific surface area and a high  $\beta\text{-PbO}_2$  content correspond best to the structural requirements for low-rate discharge (CMC type),

— high-rate discharges require a simultaneous increase and a well-balanced ratio of fine-grained structure and porosity (see the influence of CMC, silica gel), *i.e.*, neither a too high [19] nor a too low content of fine-grained  $\beta\text{-PbO}_2$ . If the surface area is too small, covering  $\text{PbO}_2$  with  $\text{PbSO}_4$  has a negative effect (carbon black type).

Thus, the effect of additives is frequently to increase the inner surface area and porosity, *i.e.*, to decrease the active material density. *A priori*, however, a decrease in the density of the active mass can be expected, since, in most cases, the specific volume of the additives is greater than that of the respective lead compounds (active material)

From this tendency an increase in the effective current density results — referred only to the active material — during formation\* and discharge, which can be compensated for only by an additional increase in porosity and surface area. From this viewpoint, the improvement in the electrical performance by additives (*e.g.*, 0.2% CMC or silica gel) is of increasing value.

A favourable influence on the utilization of the active masses also results from the ability of additives to accumulate water and electrolyte during manufacture and discharge (CMC, carbon black, silica gel) and to contribute to the formation of ionically conductive paths (fibres)

The following observations can be made concerning the mode of action of the additives investigated

— The mode of action of water accumulating additives (CMC, carbon black) consists of the improvement and increase in the water absorption of

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\*No experimental indication of this could be found

the paste, which results in a decrease of the paste density without any impairment of workability. This leads to an influence on the pore structure after curing, especially to an increase in porosity.

— The effect of additives influencing crystallization (e.g., CMC, silica gel) may be due to different mechanisms. The effects are to act as a foreign seed or protective colloid and to favour nucleus formation (silica gel) or to suppress the growth of smaller particles by mutual screening with protective colloid particles (CMC). Therefore, such additives lead directly to the formation of fine grained or coarse grained secondary structures after curing and formation.

Since the pore structure after curing immediately determines the sulphation rate during formation, the primary structure ( $\alpha/\beta$ -PbO<sub>2</sub> ratio) of the formed electrode is also influenced to a decisive degree by water-accumulating and crystallization-influencing additives.

— The use of electron conducting additives (carbon black) results especially in an improvement of the electronic conductivity of electrodes at the beginning of formation. This leads not only to a decrease in the ohmic drop, but also to an increase in the PbO/ $\alpha$ -PbO<sub>2</sub> surface area contact, resulting in a lowering of electrochemical polarizations. As a result of this, a long-term and more comprehensive  $\alpha$ -PbO<sub>2</sub> formation can take place.

It can be stated that after formation there is no direct effect\* of the types of additives mentioned on any of the electrode parameters. After 216 cycles, however, it seems possible that the primary and secondary structures still reflect the earlier influence of additives.

— A further mechanism of the action of additives consists in the mechanical stabilization of the active mass. This influence, typical of fibres, shows a long-term effect in the course of cycling, since there is little oxidation of the additive.

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\*This results also from the removal of most carbon-containing additives (carbon black, CMC, but not fibres) by oxidation.

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