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A new generation of highly efficient expander products and correlation between their chemical composition and the performance of the lead–acid battery

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Abstract

A family of eight lignosulphonates produced by Borregaard LignoTech (Norway) is investigated with the aim to determine their efficiency as expanders in the negative plates of SLI lead–acid batteries. The lignosulphonates are introduced during preparation of the paste from which the negative active mass is formed. All battery tests were performed employing the DIN43539-2 test protocol. Besides the battery tests, all lignosulphonates were characterized with regard to their chemical composition (i.e., the content of various functional groups such as –COOH, Ar–OH, $-O \cdot CH_3$ and organic sulphur in the structure of the lignins), average molecular weight and purity. It has been found that the lignins UP-393, M, D, Vaniperse-A (VS-A) and UP-414 have a very strong beneficial effect as expanders on the performance of the negative plates. It has also been established that the cycle life of the batteries is limited by the conversion of the energetic NAM structure into skeleton one. As a result of this conversion, large shapeless lead crystals were formed with small surface area and large macropores in-between. The beneficial effect of the expander has been found to correlate positively with low number average molecular weight of the lignins and their derivatives, high –COOH content, low $-O \cdot CH_3$ and organic S content, optimum Ar–OH content and high lignin purity. Expanders with different chemical composition should be selected for different battery type applications. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Organic expanders are an indispensable component of the paste recipes for lead–acid battery negative plates. These substances regulate the processes involved in the formation of the structure of the lead active mass during manufacture of the negative plates. Expanders exert a strong influence on the crystallisation processes of Pb on charge and of $PbSO_4$ on discharge [1–4,5a,5b,6,7,8a,8b,9–11]. Expanders affect also the overvoltage of hydrogen evolution thus influencing the charge processes and the self-discharge of the negative plates. Through these effects, expanders ensure higher capacity and better cold cranking ability (CCA) and cycle life performance of the batteries.

Organic expanders are mainly chemically treated lignins or derivatives of the latter. These are complex polymer substances containing different functional groups such as methoxyl, phenolic, carboxyl, ketonic, carbinol structural groups, etc. The correlation between the structural groups building the different expanders and the performance of the negative plates (e.g., capacity, CCA, cycle life, self-discharge, charge acceptance) has been the object of research for some time now. This is a very complex correlation because, on the one hand, lignosulphonates themselves contain quite a great number of structural groups occupying different positions in the structure of the expander and, on the other hand, these active groups affect in different ways the physiochemical, electrochemical and crystallisation processes involved in the formation and

disintegration of the NAM structure. Ritchie [7] has found that phenol groups have a beneficial effect on the negative plate's characteristics, the substitution of the second hydroxyl group increasing their effect in the order *ortho*, *meta*, *para*. Carboxylic and ketonic groups have little effect on the expander, whereas additives containing aldehyde groups increase its efficiency. SO_3H groups also exert a beneficial effect. Quinones and their derivatives (benzoquinone, quinhydrone, cyclohexanol, etc.) have well-pronounced expander properties [12]. The structural groups of the pyrocatechol type, which are a constituent part of the lignin structure, exert a beneficial influence on the performance of the battery [11]. A more detailed overview of the effect of structural groups contained in the lignins on battery performance is given in Ref. [13]. However, despite the results of these investigations, the correlation between expander structure and battery performance is not quite clear yet.

The most widely used expander product for SLI batteries is Vanisperse-A (VS-A), produced by Borregaard LignoTech (Norway). This company is a supplier of a great variety of lignin products manufactured in its affiliate companies in Norway, Sweden and USA. To characterise the efficiency of these lignins as expanders was the objective of the present investigation.

All lignins under test will be regarded as members of a family. The individual lignosulphonates contain different amounts of structural groups (phenolic, –COOH, methoxyl, organic sulphur). Thus, it can be established how the changes in content of a given functional group in the lignins within the family affect the different battery performance parameters. This was the second objective of the present investigation.

2. Experimental

2.1. Types of expanders under test

The effect of the following lignosulphonates on the performance of SLI batteries was investigated:

UP-393	UP-417
UP-413	M
UP-414	D
UP-416	VS-A

UP-416 is a purified softwood Kraft lignin. UP-393 is a softwood Kraft lignin sulphonate produced via a proprietary process used in Borregaard LignoTech. The sulphonic acid groups are introduced in the side chains, while most sulphomethylated lignins will have the sulphonic acid groups in the ring. UP-417 is a purified, softwood sodium lignosulphonate. UP-413 and UP-414 are desulphonated, high molecular weight (HMW) sodium lignosulphonates

made from softwood. VS-A is a purified, oxidized softwood sodium lignosulphonate with low molecular weight (LMW). M and D are purified, oxidized hardwood sodium lignosulphonates with low molecular weight. A more detailed description of the above lignosulphonates is presented elsewhere [13].

2.2. Characterization of the expanders under test by chemical composition and molecular weight

The expanders were characterised with regard to the structural groups contained and with regard to their molecular weight. The functional group content was determined in the laboratories of Borregaard LignoTech and are given as weight percentages of lignin dry weight.

Carboxylic acid (–COOH) groups were determined by a conductiometric method through titration against 0.05 M NaOH [14]. The standard deviation of this method is 0.18%.

Methoxyl groups $(-O \cdot CH_3)$ were determined by a modified Zeisel procedure [15]. This procedure is described in more details in Ref. [13].

The phenolic hydroxyl groups (Ar–OH) were determined by a UV absorption method, looking at the difference in the UV-spectra at high (> 11) and low (≈ 2.1) pH. The standard deviation of this method being 0.04%. Lignins have an absorbance maximum at 270–280 nm at low pH (2.0–2.2). K_{solid} is the absorbance maximum for a 500 ppm solution of the lignin. UV spectra were recorded on a Perkin-Elmer Lambda 2S UV-Visible spectrophotometer. Both K_{solid} and the phenolic hydroxyl group (Ar–OH) determinations are based on average molar extinction coefficients. Most contaminants in lignins do not give UV-absorption. K_{solid} is, thus, a measure of the purity of the products [16].

The sulphur in these lignins is in at least three different forms. That is, inorganic sulphur (mostly sulphate), sulphonic acid groups, and other organically bound sulphur. Inorganic sulphur was determined by precipitation with barium chloride to measure the amount of insoluble barium sulphate. Total sulphur was determined by oxidation of the sample with perchloric acid to convert all sulphur into sulphate and then it was precipitated with barium chloride [17]. Organic sulphur is calculated as the difference between the total and the inorganic sulphur. The standard deviations in the determination of sulphur is 0.1% for inorganic sulphur, and 0.3% for total and organic sulphur. The amount of inorganic sulphur is small and does not vary much between the different expanders. The variation in total sulphur is thus mostly a variation in organically bound sulphur. Kraft lignins typically contain 1.5% sulphur, although the exact nature of the sulphur species is not known [15].

Molecular weights were determined on a Jordi Glucose DVB 10000 Å column. The mobile phase consisted of

10% DMSO in water buffered with sodium hydrogen phosphate buffer and 0.1% sodium dodecyl sulphate added. A Spectra System AS3500 sample holder, P4000 pump, and UV2000 detector were used. The software allows the calculation of different molecular weight averages (M_n, M_w, M_z, and M_{z+1}) as well as polydispersity. The molecular weights are given relative to two Borregaard standards with M_w of 68,000 and 8300 Da. The relative values of the different lignins are accurate to ± 1000, while the absolute values depend on the accuracy of the standards.

2.3. Manufacture of negative plates

The negative plates were produced using leady oxide (PbO/Pb = 0.73/0.27) and H_2SO_4 s.g. 1.4 in a H_2SO_4 leady oxide ratio equal to 4.5%, the respective expanders in the respective concentrations plus 0.8% $BaSO_4$, 0.2% carbon black and H_2O. All pastes were prepared in a vacuum paste reactor supplied by Maschinenfabrik Gustav EIRICH (Germany) and then pasted over commercial SLI grids cast of Pb–1.8%Sb–0.1%As–0.2%Sn alloy. After curing and formation, the plates were dried in a nitrogen atmosphere.

The following expanders were used for paste preparation:

UP-393 (0.2%)	UP-417 (0.2%)
UP-413 (0.1%)	M (0.2%)
UP-414 (0.4%)	D (0.2%)
UP-416 (0.4%)	VS-A (0.15%)

First, the optimum concentration of a given expander was determined for this particular application. The expander concentrations in the pastes varied from 0.1% to 0.4%. The above table gives the respective expander concentrations yielding the highest battery performance characteristics.

2.4. Manufacture of lead–acid batteries

Batteries (12 V/42 A h) were assembled with cells containing four negative and five positive plates. The battery performance parameters were limited by the negative plates. In all tests, the behaviour of the negative plate potential was followed. Polyethylene gauntlet separators (Daramic-Daga, Germany) were used. All batteries were of the flooded type with H_2SO_4 s.g. 1.28.

2.5. Test methods

All batteries were set to tests following the DIN 43539-2 test protocol for SLI batteries. Two batteries of each type were tested, one of them being set to initial performance

and cycle life tests, and the other one to self-discharge and charge acceptance tests.

The initial performance tests included the following.

(a) Three C_{20} capacity measurements at 25°C.

(b) Two CCA tests at -18°C with a discharge current $I_{disch} = 5C_{20}$ A until an end-of-discharge voltage $U_{EOD} = 6$ V; the battery voltage at the 30th and at the 60th second of the CCA discharge, and the cold cranking capacity $C_{CCA} = C/0.2C_{20}$ were measured. (C is the capacity measured at -18°C vs. the $0.2C_{20}$ capacity at 25°C.)

A scheme of the cycle life tests is presented in Fig. 1. These tests were performed at 40°C. One 1-week cycle comprised 10 charge–discharge cycles. The end-of-discharge voltage at the 10th cycle was measured. Then the battery was left on open circuit at 40°C for 65 h and then a CCA test was performed.

Samples were taken from the negative active mass before and after the cycle life tests and these samples were subjected to Hg porosimetry to determine their surface and pore volume distribution by pore radius as well as to BET surface determinations and SEM observations to examine the NAM structure.

A new battery was used for the charge acceptance test. The latter comprised the following procedures: the batteries were discharged at $I_{disch} = 2I_{20}$ A at $t^o = 25 \pm 2$°C until a depth of discharge DOD = $0.5C_{20}$ was reached. Then, they were left on open circuit at $t^o = 0 \pm 1$°C for 18 h. The batteries were then charged at charge voltage $U_{ch} = 14.4 \pm 0.05$ V. The DIN43539-2 test protocol re-
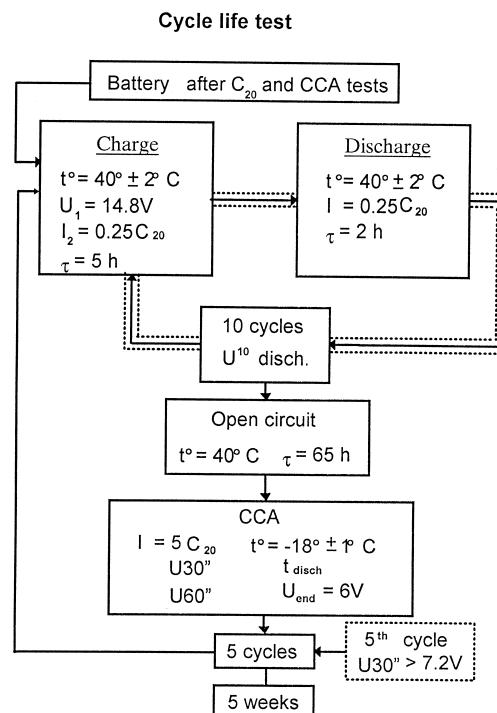
Cycle life test

Fig. 1. Schematic representation of the procedures involved in the cycle life tests.

quires that the current at the 10th minute of charge at $U = 14.4$ V is $I_{10\ \mathrm{min}} \geq 4I_{20}$ A, where I_{20} is the current at 20-h rate of discharge.

After the charge acceptance tests, the batteries were set to self-discharge tests. The charged battery was left on open circuit at $40 \pm 2°C$ for 21 days. Then, it was set to CCA tests at $I_{CCA} = 5C_{20}$ A. The DIN requirement is $U_{30''} \geq 8.4$ V. The cold cranking capacity C_{CCA} was also determined.

3. Results

3.1. Initial battery performance tests

Fig. 2 presents the capacity data obtained by the three capacity measurements (at 20-h rate of discharge) and the CCA test results given with: (a) the voltage at the 60th second of the high rate discharge at $-18°C$ at $I = 5C_{20}$ A; and (b) the cold cranking capacity $C_{CCA} = C/0.2C_{20}$ in percent.
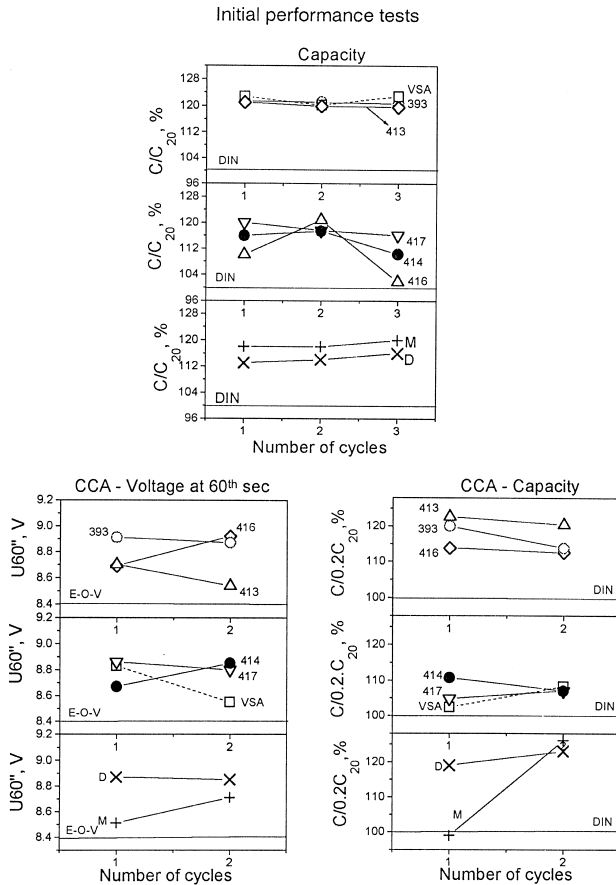

Fig. 2. Initial capacity (C/C_{20}, %) and CCA data for the voltage at the 60th second and the C_{CCA} capacity at high rate discharge with $I = 5C_{20}$ A at $-18°C$. C_{20} is the rated capacity.
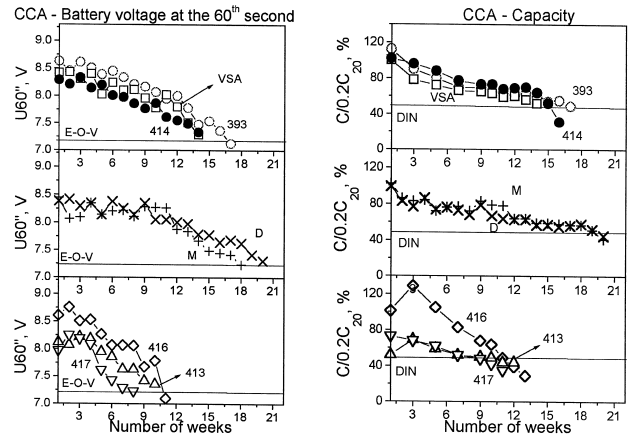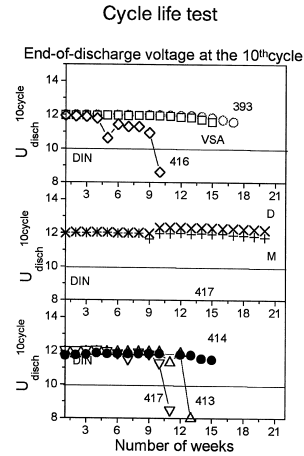

Fig. 3. End-of-discharge voltage at the 10th week cycle and CCA test after every 10-week cycles of the DIN cycle life test.

All batteries under test meet the requirements of the DIN standard and a ranking of the expander effect on the battery performance can be made. The ranking is made on grounds of the average values obtained from the three C_{20} capacity measurements. The average values are ranked in descending order and thus the efficiency of the expanders is evaluated.

A similar ranking is also made with regard to the expander efficiency on the CCA performance of the battery: ($U_{60''}$ and $C_{CCA} = C_{-18°C}/0.2C_{20}$, %). The following classification of the expanders under test is obtained:

Capacity: VS-A > UP-393 > UP-413 > M > UP-417 > UP-414 > D > UP-416

CCA $U_{60''}$: UP-393 > D > UP-417 > UP-416 > UP-414 > VS-A > UP-413 > M

C_{CCA}: UP-413 > D > UP-393 > UP-416 > M > UP-414 > UP-417 > VS-A.

3.2. Cycle life tests

Fig. 3 presents the end-of-discharge voltage at the 10th week cycle and the CCA test results ($U_{60''}$ and $C_{CCA} =$
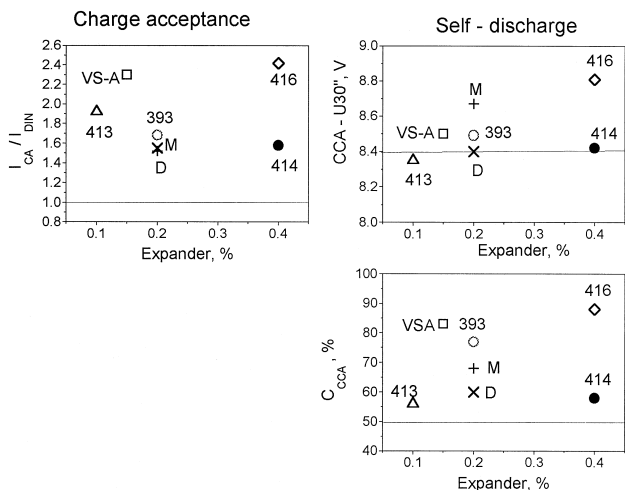
Fig. 4. Charge acceptance and self-discharge test results.

Table 2

Overall ranking points	Expander	$\sum N_i$
1	UP-393	26
2	D	32
3	M	35
4	VS-A	36
5	UP-416	39
6	UP-414	46
7	UP-413	48
8	UP-417	

Based on the above results, the following classification of the influence of the expanders on the S.D. and Ch.A. performance can be made:

Ch.A.: UP-416 > VS-A > UP-413 > UP-393 > UP-414 > D > M

S.D. $U_{30''}$: UP-416 > M > VS-A > UP-393 > UP-414 > D > UP-413

S.D. C_{CCA}: UP-416 > VS-A > UP-393 > M > D > UP-414 > UP-413

3.4. Final ranking of the expanders with regard to their effect on the battery performance parameters

The classifications made in Sections 3.1, 3.2 and 3.3 above show that the expanders affect the different battery parameters in different ways. One expander product may have a strong influence on one battery parameter but affect only slightly another parameter [18]. Hence, it is essential to make an overall assessment of the expander efficiency. However, the different battery parameters are measured in different units. An overall ranking can be made on grounds of the ranking positions occupied by the expanders when their effect on the different battery parameters is assessed. Table 1 summarises the ranking positions occupied by the expanders under test when classified according to their beneficial effect on the initial performance parameters, the cycle life, the self-discharge and the charge acceptance of the batteries. The number N_i corresponds to the position

$C/0.2C_{20}$, %) obtained. The required cycle life according to the DIN standard is 5-week cycles. All batteries under test meet the above requirement, some of them enduring twice and even three times longer.

The ranking of the expanders with regard to their effect on the various cycle life parameters is as follows:

$U_{\text{disch}}^{10\text{th cycle}}$: D = M > UP-393 > VS-A > UP-414 > UP-413 > UP-417 > UP-416

CCA, $U_{60''}$: D = M > U-393 > UP-414, VS-A > UP-416 > UP-413 > UP-417

C_{CCA}: M > D > UP-393 > UP-414 > VS-A > UP-416 > UP-413 > UP-417.

3.3. Charge acceptance and self-discharge tests

Fig. 4 shows the charge acceptance (Ch.A.) and self-discharge (S.D.) data obtained for the batteries under test. The battery with UP-417 expander was not set to the above tests.

Table 1

Summary of the ranking positions occupied by the expanders under test, when classified according to their beneficial effect on the battery performance parameters

Ranking points N_i	Initial performance parameters			Cycle life performance parameters			Charge acceptance (Ch.A.)	Self-discharge	
	C_{20}	$U_{60''}$ CCA	C_{CCA} CCA	$U_{10\text{ disch}}$	CL $U_{60''}$	CL C_{CCA}		S.D. $U_{30''}$	S.D. C_{CCA}
1	VS-A	UP-393	UP-413	D	D	M	UP-416	UP-416	UP-416
2	UP-393	D	D	M	M	D	VS-A	M	VS-A
3	UP-413	UP-417	UP-393	UP-393	UP-393	UP-393	UP-413	VS-A	UP-393
4	M	UP-416	UP-416	VS-A	UP-414	UP-414	UP-393	UP-393	M
5	UP-417	UP-414	M	UP-414	VS-A	VS-A	UP-414	UP-414	D
6	UP-414	VS-A	UP-414	UP-413	UP-416	UP-416	D	D	UP-414
7	D	UP-413	UP-417	UP-417	UP-413	UP-413	M	UP-413	UP-413
8	UP-416	M	VS-A	UP-416	UP-417	UP-417			

occupied by a given expander in the ranking of its efficiency with regard to a given battery parameter (e.g., #1 = 1 point; #2 = 2 points, #3 = 3 points). Then the ranking points gained by a given expander in the different battery tests are summed up ($\sum N_i$).

The overall ranking (OR) of the expanders under test made on grounds of the $\sum N_i$ value is given in Table 2. The ascending order of the $\sum N_i$ values corresponds to a descending order of the beneficial effect of the expanders on battery performance. The lignins with the most beneficial effect on the performance of the negative plates are:

$$UP - 393 > D > M > VS - A.$$

3.5. Specific BET surface and pore volume of the NAM before and after the DIN cycle life tests

Samples were taken from the negative active mass after formation of the negative plates and at the end of battery life. These NAM samples were subjected to porosimetry and BET surface measurements. The obtained BET surface data are presented in Table 3.

The data indicate that the BET surface of NAM decreases twice to three times with cycling. The greatest decrease in specific surface is observed with the NAM containing UP-393, VS-A and UP-413.

Table 4 presents the NAM pore volume data obtained before and after the cycle life test. Except for the NAM with UP-414, the total pore volume of all other plates increases by 10% to 30%. The most pronounced expansion in volume is observed with the NAMs containing UP-416 and M.

The data in Tables 3 and 4 show that the BET surface area decreases and the total pore volume increases on cycling, which indicates that the lead crystals in the NAM grow in size and so does the volume of the pores in-between.

3.6. Changes in NAM structure on cycling and expander influence

As established earlier [19–21], the NAM structure consists of a skeleton formed during the first stage of forma-

Table 3
BET surface area before and after the DIN cycle life test

Expander type	Specific surface S^1 [m^2/g] before cycling	Specific surface S^2 [m^2/g] after cycling	S^1/S^2
VS-A, 0.15%	0.540	0.200	2.70
UP-393, 0.2%	0.660	0.230	2.87
UP-416, 0.4%	0.790	0.480	1.65
UP-413, 0.1%	0.350	0.130	2.69
UP-414, 0.4%	0.410	0.220	1.87
D, 0.2%	0.530	0.272	1.95
M, 0.2%	0.570	0.382	1.49

Table 4
Total pore volume in NAM before and after the DIN cycle life test

Expander	Total pore volume V_{por}^1 [cm^3/g] before cycling	Total pore volume V_{por}^2 [cm^3/g] after cycling	V_{por}^2 / V_{por}^1
VS-A, 0.15%	0.1310	0.1454	1.11
UP-393, 0.2%	0.1335	0.1613	1.21
UP-416, 0.4%	0.1362	0.1786	1.31
UP-413, 0.1%	0.1284	0.1443	1.12
UP-414, 0.4%	0.1146	0.0967	0.84
D, 0.2%	0.1100	0.1370	1.25
M, 0.2%	0.1135	0.1470	1.30

tion and energetic structure (small Pb crystals) formed on the surface of the skeleton during the second stage of formation of NAM. The energetic structure and part of the skeleton of NAM are involved in the charge and discharge processes. On cycling of the battery, the energetic structure can be converted into skeleton one, which leads to capacity decline, or vice versa, the skeleton structure can be converted into energetic one, which results in capacity increase. However, very soon the contact between the individual crystals is impaired and the capacity declines, which limits the life of the battery. Through scanning electron microscopy, we observed the changes in the energetic structure on cycling of plates with different expanders. The skeleton structure cannot be seen directly as the skeleton is covered by the crystals of the energetic structure. To be able to examine the NAM skeleton, the plate should be discharged and the obtained $PbSO_4$ dissolved. SEM micrographs of the NAM of plates with UP-393, UP-414 and VS-A before and after cycling are presented in Figs. 5–7, respectively, at magnifications of $1000 \times$ and $10,000 \times$.

Two basic conclusions can be drawn from the SEM micrographs.

(a) The size and morphology of the lead crystals comprising the energetic structure are greatly influenced by the type of expander used. This is most evident when comparing the photographs of the NAM structures with the three expanders before cycling at magnification $10,000 \times$ (Figs. 5b, 6b and 7b). A similar variety of energetic structures were also observed with the NAM of plates prepared with the other five expander products.

(b) A several-fold increase in size of the lead crystals of the energetic structure of NAM is observed after cycling. These crystals become analogous in shape and size to those of the skeleton structure. Similar changes are also observed with the NAM with the other five expanders under test. So it can be generally concluded that the energetic structure comprising relatively small crystals is converted into skeleton structure built of large, shapeless interconnected crystals.

The above conclusions are in perfect agreement with the data presented in Tables 3 and 4. On cycling of the battery, the total pore volume increases, whereas the BET surface decreases. Consequently, the capacity declines
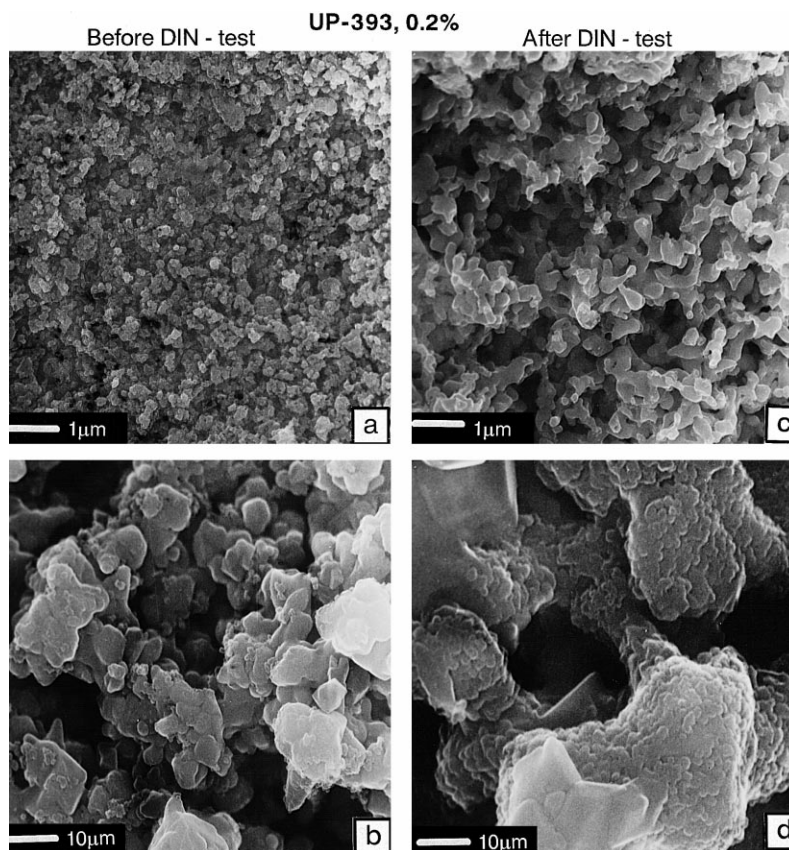
Fig. 5. Structure of the NAM containing expander UP-393: (a and b) before cycling, and (c and d) after cycling; (a and c) $1000 \times$ magnification, (b and d) $10,000 \times$ magnification.

reaching a value assumed to be the end-of-life criterion. It can be expected that the different expanders will have different chemical stability. Hence, the process of lignin disintegration will proceed at different rates, which will result in different rates of conversion of the energetic structure into skeleton one. This, in turn, will yield different cycle life span of the negative plates with different expanders. This relationship is illustrated in Fig. 3.

3.7. Chemical composition and molecular weight of the expanders under test

These determinations were performed in the laboratories of Borregaard LignoTech.

Table 5 summarises the analytical data for the chemical composition of the expanders under test as well as the K_{solid} and average molecular weight data.

If we look at the data in the weight average molecular weight row in Table 5, we can divide the expanders belonging to this family into two groups:

(a) Expanders with lower molecular weight (LMW), when their average molecular weight is smaller than 30 kDa. These include: VS-A, D, UP-416, UP-393 and M.

(b) Expanders with HMW, when their average molecular weight is higher than 30 kDa. These include: UP-417, UP-414 and UP-413.

Fig. 8 illustrates the correlation between the organic sulphur content in the lignins and their molecular weight M_w. It can be seen that LMW lignins have low organic sulphur content $(1.1–3.4\%)$, whereas HMW lignins contain greater amounts of organic sulphur $(4.9–6.2\%)$. Hence, in some cases, the observed correlation between expander's molecular weight and battery performance is actually a result of the combined effect of M_w and organic sulphur content.

The data in Table 5 show that the different lignins contain different amounts of the various structural groups: methoxyl, phenolic OH, –COOH and organic S. This difference in chemical composition would affect the structure of the NAM formed and hence the battery performance parameters.

3.8. Correlation between the number average molecular weight (M_n) and the overall ranking (OR) of the expanders' efficiency

Fig. 9a shows the ascending order of the expanders under test with regard to their number average molecular
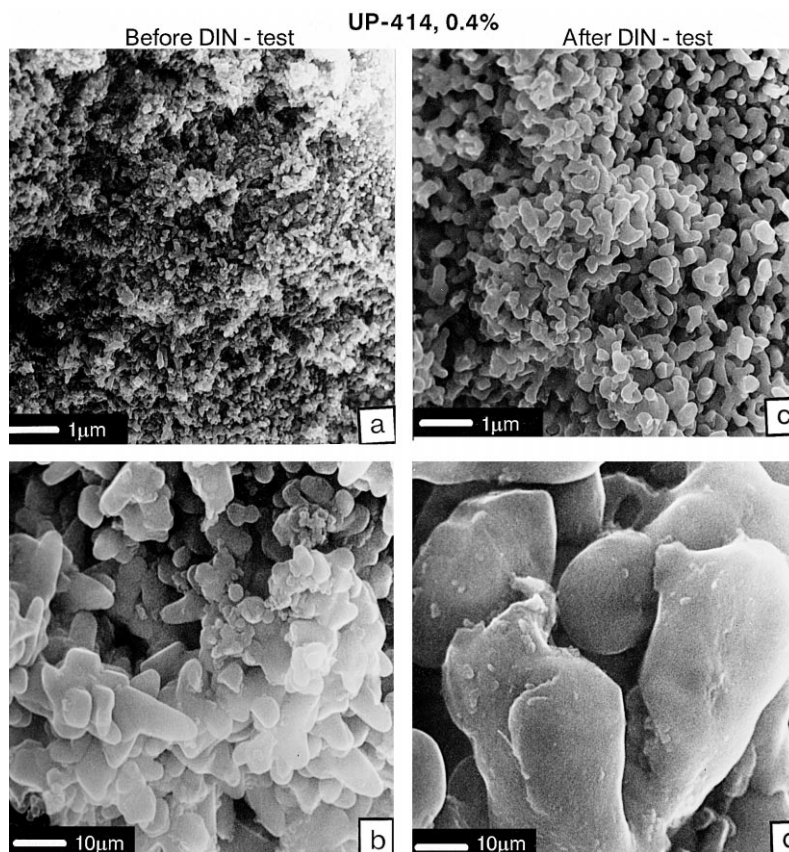
Fig. 6. Structure of the NAM containing expander UP-414: (a and b) before cycling, and (c and d) after cycling; (a and c) $1000 \times$ magnification, (b) and (d) $10,000 \times$ magnification.

weight (M_n). Fig. 9b illustrates the decline in the beneficial effect of the expanders on battery performance as evidenced by the overall expander ranking ($\sum N_i$) (the data are taken from Table 2).

The arrangement of the expanders in both figures is very similar. The only exception is expander UP-416, which has the lowest molecular weight (first position in the molecular weight sequence) but occupies the fifth place in the overall ranking ($\sum N_i$). UP-416 is the only unmodified Kraft lignin. UP-416 has no sulphonic acid groups (organic S is contained in some other form), and it falls outside the general trend for the other expanders which all have some sulphonic acid groups in their structure. The number average molecular weight (M_n) can serve as a criterion, though not an absolute one, for the selection of appropriate expander products for SLI batteries. A good expander should have low M_n.

M_n depends directly on the number of polymer species in the solution. Osmotic pressure of a polymer solution, boiling point elevation, freezing point depression and vapor pressure lowering all depend on the M_n. For all these properties that depend directly on the number of species in solution the contribution from the HMW polymers is small compared to that from the low molecular species.

There is a strong correlation between the organic sulphur content and M_n (correlation coefficient 0.93). This means that it is impossible to decouple the effects of sulphur content and molecular weight. More sulphur would mean more sulphonic acid groups, and thus a better solubility. A more soluble compound would be less inclined to stick to the surfaces, and thus have less surface activity.

It can be seen from Fig. 9a and b that the expanders with low average molecular weight (M_w) have the strongest beneficial effect on battery performance. Smaller molecules adsorb to the surface of a hard phase faster than polymer molecules with higher molecular weight. Smaller molecules are more mobile and have a better chance of sticking to surface. During charge–discharge cycling the NAM of the battery is a dynamic system. Consequently, mainly LMW polymer molecules are adsorbed to the surface of the lead nuclei and crystals. That could be the reason for the more pronounced beneficial effect of the expanders with LMW as compared to higher molecular weight products (Fig. 9).

It has been found that the polymer fractions with higher molecular weight are adsorbed preferably to the lead surface under equilibrium conditions [22]. A large molecule has many points of contact with the surface and sticks more strongly to it. On the other hand, a larger polymer
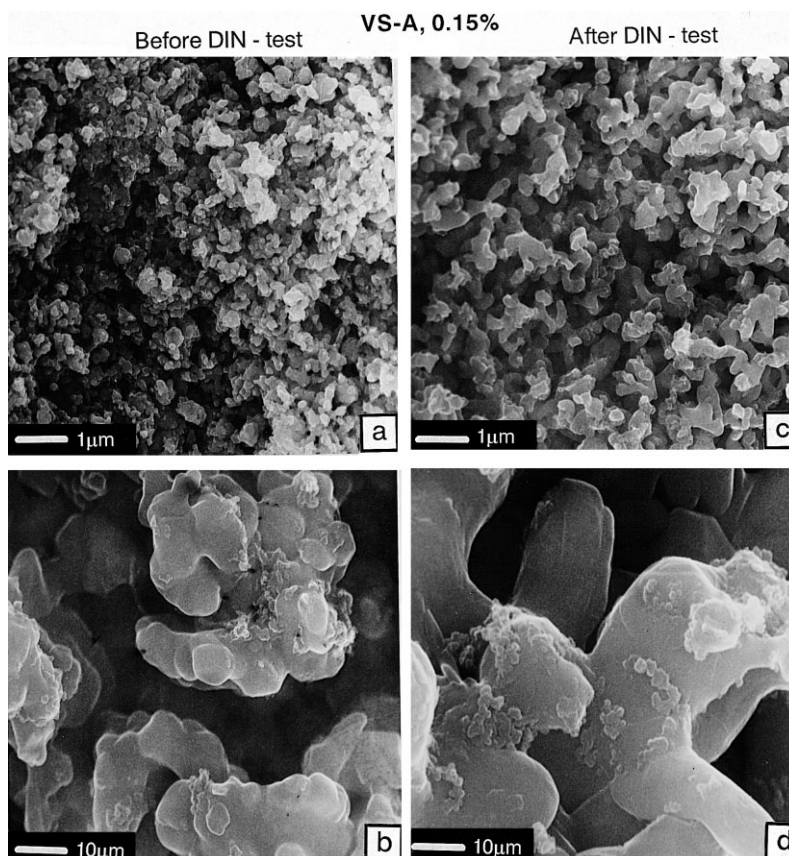
Fig. 7. Structure of the NAM containing expander VS-A (0.15%): (a and b) before cycling and (c and d) after cycling; (a and c) 1000 × magnification, (b and d) 10,000 × magnification.

molecule has less freedom in solution than several smaller molecules. Hence, first smaller polymer molecules will be adsorbed to the lead surface and then these molecules will gradually be substituted by larger ones. On grounds of this finding it can be supposed that, due to the above processes, the beneficial effect of the expanders on the performance of stationary batteries will differ from their influence on SLI batteries. Stationary batteries operate in a buffer charging mode for a long period of time, which allows larger

polymer chains (molecules) to be adsorbed to the lead surface.

3.9. Correlation between the content of different structural groups in the expanders and the performance of the battery

An attempt was made elsewhere to find a correlation between the basic lignin characteristics and the battery

Table 5
Properties of the lignins used in this investigation

Property	UP-393	UP-414	VS-A	UP-416	UP-413	UP-417	M	D
Methoxyl, % w/w	9.4	10.5	12.3	11.2	10.0	8.3	12.3	10.8
Phenolic OH, % w/w	2.01	2.02	1.61	0.78	1.76	1.56	2.6	2.4
Inorganic S, % w/w	0.50	0.52	0.47	0.43	0.23	0.76	0.34	0.55
Organic S, % w/w	1.4	5.5	2.5	1.1	5.9	6.2	2.4	3.5
Total S, % w/w	1.9	6.0	3.0	1.5	6.1	7.0	2.7	4.0
Carboxylic acid, % w/w	12.6	6.66	11.2	11.7	8.96	8.15	8.5	8.4
K_{solid}	19.9	15.3	n.a.	16.0	13.6	9.61	22.2	18.2
M_n, kDa	3.62	6.37	5.01	2.08	6.84	7.17	4.6	4.1
M_w, kDa	25.6	78.0	15.6	24.8	81.0	50.9	29.6	23.2

$M_n = (\Sigma_i n_i M_i)/(\Sigma_i n_i)$; number average molecular weight. It gives the number of the polymer chains with average molecular weight.
$M_w = (\Sigma_i n_i M_i^2)/(\Sigma_i n_i M_i)$; weight average molecular weight. Gives the average molecular weight.
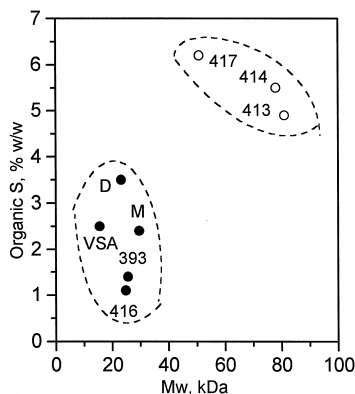
Fig. 8. Correlation between organic sulphur content and molecular weight of the lignins.

Carboxyl groups (- COOH)

Fig. 10. Correlation between the –COOH group content in the lignins and: (a) the capacity C_{20} in percent (vs. the rated capacity C_0); and (b) the C_{CCA} capacity after self-discharge of the battery.

performance parameters through PCA analysis [13]. It turned out that such a multivariate analysis leads to a very complex correlation. Therefore, in the present investigation, we have tried to simplify the task.

Investigating a family of eight lignin products allowed us to study the correlation between the content of a given functional group in the lignins (Table 5) and a given battery performance parameter. If we plot the quantity of a given functional group in the lignins on the abscissa of a coordinate system and the battery performance parameter on the ordinate, we will obtain two types of patterns. The first type features chaotic distribution of the batteries with different expanders, which indicates that there is no correlation between the content of the given functional group and the given battery performance parameter. The second type of dependence features a curve, which is an evidence of the correlation between the content of the given functional group in the expander and this battery performance parameter. Relationships of the second type will be discussed below.

3.9.1. Carboxylic acid groups (–COOH)

A correlation was found between the initial capacity and the capacity after self-discharge ($C_{CCA} = C_{SD}/0.2 C_{20}$) on the one hand, and the content of –COOH groups in the lignins on the other hand. These relationships are presented in Fig. 10. The expanders with low molecular weight are marked with (●) and those with higher molecular weight, with (○).

An increase in carboxylic acid group content in the expander is related to an increase in capacity. Expanders UP-414 and D are exceptions to this trend. The curve reaches saturation at $C = 120–122\%$. Probably, this is the maximum capacity that could be delivered by the plate as an electrochemical system without causing it to rapidly disintegrate.

The cold cranking capacity after self-discharge increases almost linearly with increase in the –COOH content in the expander. This implies a positive correlation between the –COOH content and the self-discharge processes, the latter being slowed down by expanders with higher –COOH content. A notable deviation from this tendency is observed with expanders UP-393 and UP-413.
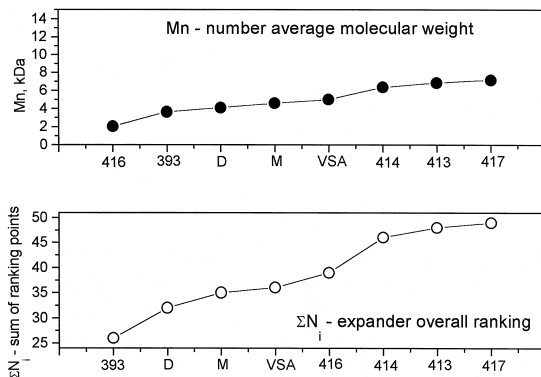

Fig. 9. (a) Expander ranking with regard to number average molecular weight. (b) Expander ranking with regard to their beneficial effect on battery performance (measured by the sum of ranking points ΣN_i gained in the different battery tests). The greater the sum ΣN_i, the weaker the beneficial effect of the expander.
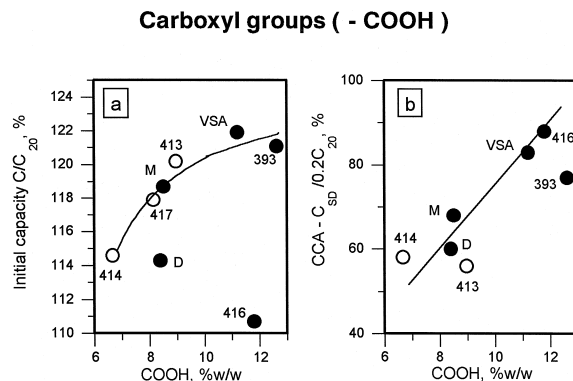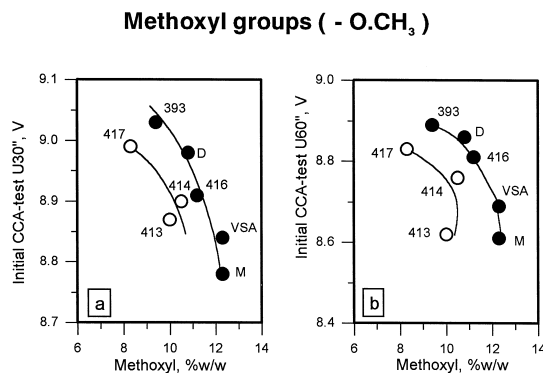
Methoxyl groups (- O.CH$_3$)

Fig. 11. Correlation between the –O·CH$_3$ group content in the lignins and the battery voltage at: (a) the 30th second; and (b) the 60th second of discharge at $I = 5C_{20}$ A at $-18°C$. (●) Expanders with low average molecular weight, (○) expanders with high average molecular weight.
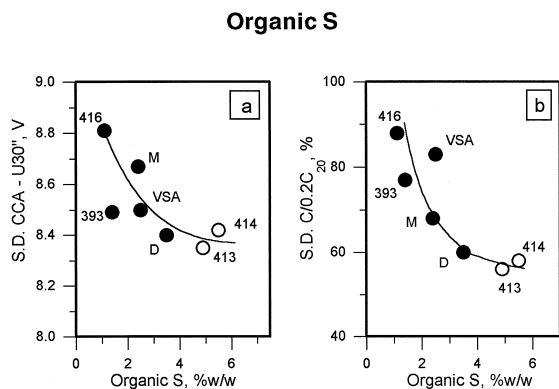
Organic S

Fig. 12. Influence of organic sulphur content in the lignins on the self-discharge processes: (a) voltage at the 30th second of CCA discharge; and (b) $C_{CCA} = C_{SD}/0.2C_{20}$.

3.9.2. Methoxyl groups ($-O \cdot CH_3$)

Methoxyl groups give a more hydrophobic character to the expanders. This affects the voltage at the 30th and at the 60th second of discharge at $-18°C$. These dependencies are presented in Fig. 11.

Expanders with higher methoxyl group content seem to have an adverse effect on the initial CCA performance, i.e., the voltage at both the $30''$ and at the $60''$ decreases. The effect of the $-O \cdot CH_3$ group content on battery performance is combined with that of the molecular weight

M_w. Two similar curves are obtained for the LMW and HMW lignins. As evident from Fig. 8, LMW lignins have low organic S content against high organic S content in HMW expanders. Hence, the observed two dependencies may be due not only to the difference in molecular weight, but also to the different organic sulphur contents in the lignins. The sulphonic groups increase the solubility of the lignins. Thus, within the group of expanders with equal $-O \cdot CH_3$ group content, those containing smaller amounts of organic S would yield higher $U_{30''}$ and $U_{60''}$ performance of the batteries in the initial CCA tests.

3.9.3. Organic sulphur

The strongest influence of the organic S content is evidenced with the self–discharge processes. Fig. 12 presents the relationship between the organic S content and the $U_{CCA}^{30''}$ and $C/0.2C_{20}$ values on discharge with $I = 5C_{20}$ A at $-18°C$ after self-discharge of the batteries. The higher the organic S content in the expanders the higher the rate of the self-discharge processes leading to a decrease in C_{CCA} and $U_{CCA}^{30''}$. A certain deviation from this tendency is observed with VS-A with regard to the C_{CCA} performance and with UP-393 with regard to the $U_{CCA}^{30''}$ performance.

Fig. 8 shows that expanders UP-413, UP-414, and UP-417 are HMW lignins and have high levels of sulphur.
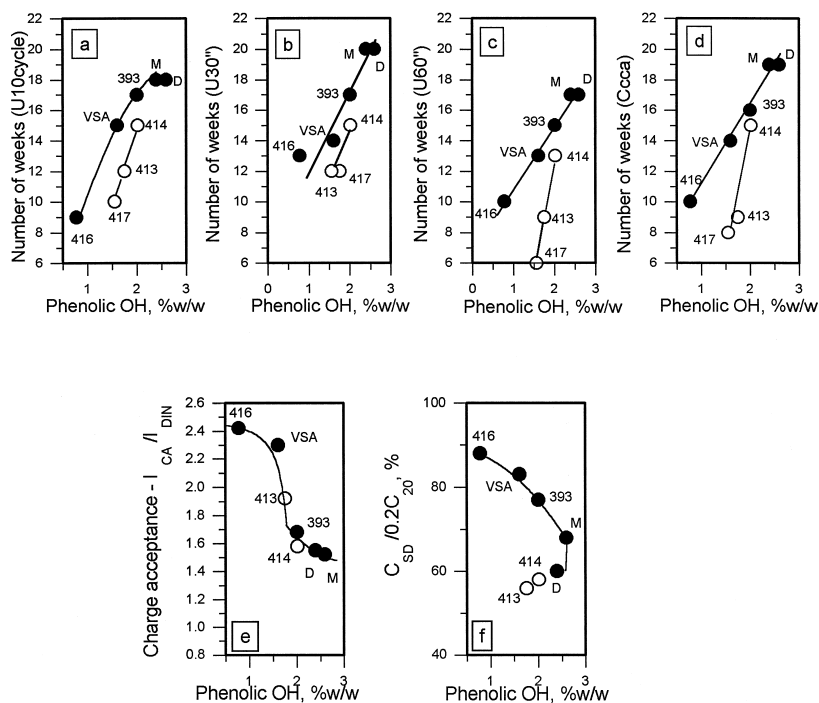
Phenolic group Ar - OH

Fig. 13. (a, b, c, d) Correlation between phenolic OH group content in the lignins and battery cycle life; (e) charge acceptance as a function of phenolic OH group content; and (f) self-discharge capacity as a function of phenolic OH group content.

The latter is mostly in the form of sulphonic acid groups ($-SO_3H$). In LMW expanders, the form of sulphur varies. Thus, for UP-416 the form of the sulphur is unknown for all of it (1.1%), for UP-393 about half the sulphur is in unknown form and half as sulphonic acids. For the rest of the LMW lignins group the majority of the sulphur is in sulphonic acid groups, but an appreciable amount is also present in an unknown form. Probably, these different forms of the organic sulphur in LMW lignins are responsible for the deviations in the curves for some of the LMW expanders in Fig. 12.

3.9.4. Phenolic groups Ar–OH

Phenolic groups affect the cycle life performance, the charge acceptance and the self-discharge of the negative plates. The relationships of these parameters to the Ar–OH content in the expanders under test are presented in Fig. 13.

The effect of Ar–OH content on the life span of the battery (measured by $U_{disch}^{10th\ cycle}$, $U_{CCA}^{30''}$, $U_{CCA}^{60''}$, C_{CCA}) is more pronounced with LMW expanders (Fig. 13a–d). The higher the Ar–OH content in the lignins, the longer the cycle life of the negative plates when cycled according to the DIN43539-2 test protocol. This beneficial effect of Ar–OH groups on the cycle life performance of SLI batteries is in agreement with most previous studies [7,23].

The opposite correlation is observed between the content of Ar–OH groups in the lignins and the charge acceptance (Fig. 13e) and self-discharge (Fig. 13fFig. 14) performance. The higher the Ar–OH content the lower the charge acceptance and the faster the self-discharge of the negative plates.

The data in Figs. 12 and 13 indicate that the organic S content and phenolic OH groups have a negative influence on the self-discharge, accelerating the latter and thus leading to a decline in the $C_{SD}/0.2C_{20}$ capacity. Fig. 14 presents the correlations between the $U_{SD}^{30''}$ and $C_{SD}/0.2C_{20}$
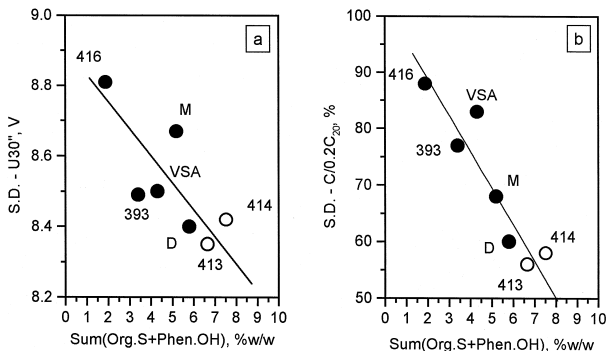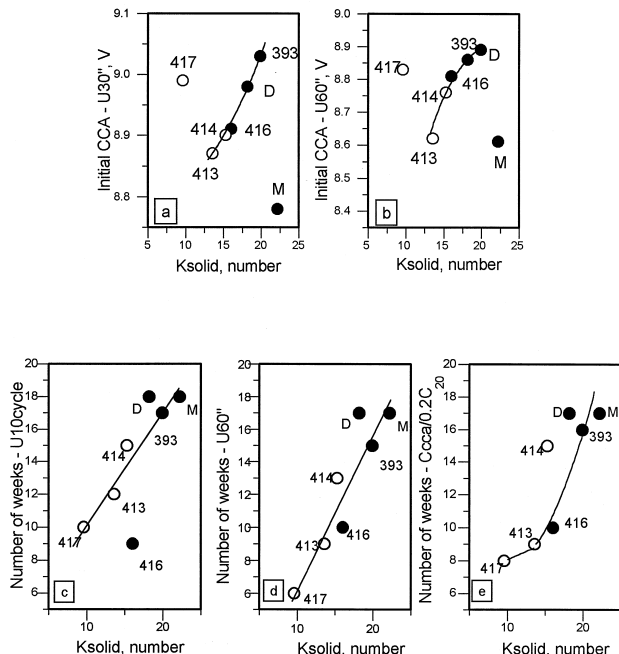

Fig. 15. Correlation between lignin purity (expressed by K_{solid}): (a and b) battery voltage at the 30th and at the 60th second of discharge during the initial CCA tests; (c) end-of-discharge voltage at the end of the 10th week cycle; (d) number of week cycles until EOD = 7.0 V at the 60th second of CCA discharge; and (e) number of week cycles until C_{CCA} = 50%.

values (in percent) and the organic S + phenolic OH group content.

The obtained curves indicate that there is a linear negative dependence between the self-discharge parameters and the (S_{org} + PhenOH) content.

This contradictory effect of the Ar–OH groups on the cycle life, charge acceptance and self-discharge of the batteries calls for finding an optimum Ar–OH content in the expander. The lignin UP-393 seems to be an example of such an optimum Ar–OH content.

3.9.5. K_{solid}

K_{solid} is a measure for the purity of the lignins. It has been established that the cold cranking discharge voltage both, in the initial performance and the cycle life tests, depends on the purity of the expander. These dependencies are presented in Fig. 15.

The higher the K_{solid} value (i.e., the purer the lignin), the higher the CCA performance parameters and the longer the cycle life of the negative plates. The only exceptions to this tendency are expanders M and UP-417 for the initial CCA measurements (Fig. 15a and b), and UP-416 for the end-of-discharge voltage after the 10th week cycle (Fig. 15c). It can be generally concluded that expanders with high K_{solid} value ensure high CCA discharge voltage.

Fig. 14. Relationship between the self-discharge parameters ($U_{SD\ 30''}$ and $C_{SD}/0.2C_{20}$, %) and the content of phenolic OH groups and organic sulphur in the lignins.

4. Conclusions

(1) It has been established that UP-393, D, M and UP-416 have beneficial effect on battery performance, similar or better than that of VS-A.

(2) The end-of-life of the negative plates is determined by conversion of the energetic structure of NAM into skeleton one, whereby the BET surface of NAM decreases and the total pore volume increases considerably.

(3) It appears to be an advantage for the beneficial effect of organic expanders on SLI battery performance if they have low number average molecular weight, high –COOH content, low content of $-OCH_3$ and organic S, optimum Ar–OH content and high purity.

(4) Lignins with different chemical composition should be selected for different battery type applications.

Acknowledgements

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