Electrochemical techniques for the characterisation of expander materials

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Abstract

Characterisation of expander materials has been obtained by comparing the results of three different electrochemical techniques: cyclic voltammetry, potentiostatic transients and electrochemical impedance. It is shown that the evaluation of the expanders' performance carried out on the basis of the results of such techniques takes into account different important actions of the organic additives such as adsorption on lead and kinetics of electrochemical reactions. Seventeen different organic substances have been tested including both commercial materials used in the lead-acid battery industry, and other materials presenting physico-chemical similarities to known expanders. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemical techniques; Electrocrystallisation; Lead-acid batteries; Expanders

1. Introduction

It is well known that the performance of the negative plates of lead-acid batteries is strongly influenced by the presence of organic substances, usually referred to as expanders, added to the negative active material during manufacturing. The effects of such additives mainly concern the performance at high rate of discharge and cyclability, but they also exert other beneficial actions on the overall behaviour of the negative plate.

Although the mechanism of action of the expanders is very complex and not yet completely understood, it is commonly accepted that adsorption of such substances on crystals is of fundamental importance for their behaviour [1–6]. In fact, the expanders adsorbed on lead seem to favour a dissolution–precipitation mechanism for lead sulphate formation, thus preventing passivation by a solid state reaction, [7–11]. According to Ritchie [4,5], who bases his considerations on ideas already expressed by Willihnganz [3], the effects of expanders are simply explained by considering that a more porous lead sulphate is

formed during discharge as a consequence of the partial coverage of the lead surface by adsorption of the organic substance, while a limitation of the size of lead crystals occurs during charge.

As already mentioned, the presence of organic expanders can also influence other aspects of the behaviour of the negative plate. In fact, the adsorption of such substances on lead modifies the electrochemical cathodic behaviour of lead by affecting the hydrogen evolution reaction, thus yielding a possible inhibiting action on the effects of impurities [12–16]. It is not clear from literature work whether adsorption of organic expanders on lead sulphate may affect the lead electrode kinetics, but according to direct measurements carried out by Sharpe [6], adsorption on lead sulphate appears to be unimportant. The effects of the expanders are highly influenced by the temperature, for temperatures above 50°C the effects of the expanders become very small [17].

Among the various electrochemical techniques which have been used for investigating the expanders, those based on cyclic voltammetry, on potentiostatic transients and on impedance measurement are of particular interest and will be shortly reviewed.

In the present work a set of seventeen different organic substances has been tested according to the just mentioned

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Table 1
List of tested expanders

Abbreviation	Expander	Description
DIW	Diwatex XP-9	Sodium salt of sulphonated kraft lignin derived from softwood
VAN	Vanisperse A	Sodium oxylignin derived from fermented spruce wood sulphite liquor
DAR	Darvan 1	Sodium salt of polymerized alkylnaphthalene sulphonic acid
QUE	Quebracho ATO	Vegetable extract from a South American tree, genus Schinopsis, relatively rich in tannin
MIM	Mimosa ME	Vegetable tanning material obtained from the bark of the black wattle
B75	B-75	Product from the condensation of urea and phenol
P63	P-63	Condensation product from naphthalene sulphonic acid
ESK	EZE-Skitan	Synthetic product obtained from the condensation of lignosulphonic acids with phenols through formaldehyde
IND	Indulin AT	A purified form of kraft pine lignin with no sulphonate groups
KRA	Kraftplex	Sodium lignosulphonate made from waste pulp liquors
HUM	Humic acid	The fraction of humic substances that is not soluble in water under acid conditions
UP298	UP298	A modified Vanisperse-A
NBNa	NBNa	Sodium lignosulphunate hardwood lignin
S004	S-004	Sodium lignosulphunate
N17	N17	Sodium lignosulphunate
DD5	DD5	Kraft lignosulfonate, condensed naphthalene sulfonate blend
DD8	DD8	Kraft lignosulfonate, condensed naphthalene sulfonate blend

three techniques, with the aim of obtaining an overall characterisation of the expander materials accounting for the different actions they exert on the lead electrode. A rather vast selection of organic substances has been considered, including both commercial materials used in the lead-acid battery industry, and other materials presenting physico-chemical similarities with respect to known expanders.

1.1. Cyclic voltammetry

An interesting method for comparing the expanders' behaviour based on cyclic voltammetry has been reported [18]. A lead electrode is cycled within the potential range -1.3 to 0.7 V (VS $Hg/Hg_2 SO_4$ electrode) with a sweep rate between 2 and 20 mV/s, the anodic amount of charge is recorded and the data are analysed to obtain information on the "efficiency" and "stability" of the tested expander.

As far as the voltammetric curves are concerned, it must be observed that a low value of the scan rate em-

ployed in the application of this method is required to remain within the limits of applicability of the mathematical approach described by Mac Donald [19] on the basis of the theory of passivity proposed by Muller [20].

The computation carried out by Mac Donald [19] shows that, in the case of an electrode on which a resistive layer is formed, the trend of a voltammetric curve $i(V)$, traced by a linear potential scan, depends on the changes of the layer resistance. According to such theory the voltammetric curves should be linear, their slope depending on the porosity and thickness of the layer which is being formed. In the case of lead in sulphuric acid the changes of the contact resistance are caused by the lead sulphate layer. The value of the current peak in the anodic branch appears to be proportional to the square root of the potential scan-rate.

According to this model, the voltammetric curves are characterised by a pronounced asymmetry because a drastic fall of the current intensity occurs when the coverage of the electrode surface by the resistive layer approaches unity. The method was employed by Hampson and Lake-
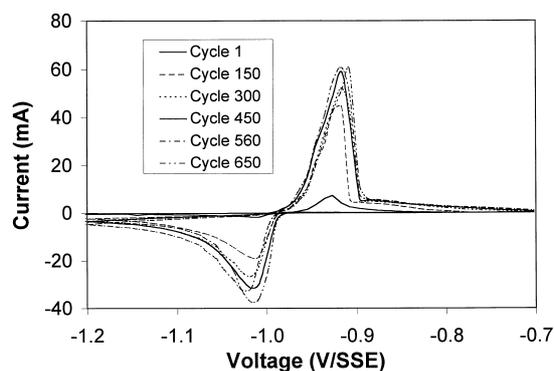
Fig. 1. Cyclic voltammograms of a pure lead electrode in 1.25 g cm^{-3} density sulphuric acid.
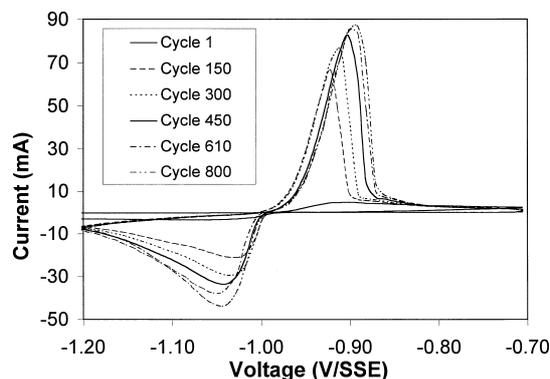
Fig. 2. Cyclic voltammograms of a pure lead electrode in 1.25 g cm^{-3} density sulphuric acid containing 20 ppm of Vanisperse A.
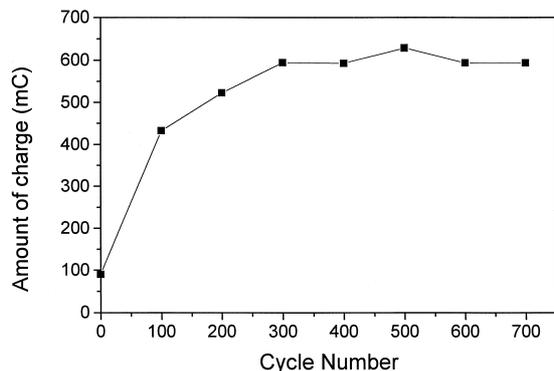
Fig. 3. Amount of charge of the anodic peak vs. number of cycles for a pure lead electrode in 1.25 g cm^{-3} density sulphuric acid.

man [21] for lead in sulphuric acid to show the effect of the potential scan-rate on the characteristics of the anodic layers. The experimental curves obtained by cyclic voltammetry are not similar to those expected by the Muller model, particularly for the first cycle. Hampson, who carried out rather wide potential scans, attributed such difference to the formation of a second phase. An alternative model, with respect to the previous one, to describe the voltammetric curves for lead in sulphuric acid has been proposed by Varela et al. [22].

By considering the values Ip and Ep of the anodic peak current it should be possible to obtain, as indicated by Hampson and Lakeman [21,23], the porosity and thickness of the sulphate layer in the presence and in the absence of the expanders.

By accepting the validity of the law for two-dimensional growth with instantaneous nucleation, it is easy to compute the mathematical expression of voltammetric curve $i(V)$.

If η is the electrodic overvoltage and u the potential scan-rate, the equation of the voltammetric curve for the formation of a layer obeying instantaneous nucleation and two-dimensional growth is given by:

$$i = a\frac{\eta}{u}\exp\left[-b(\eta/u)^2\right]$$

where a and b, as shown by Varela et al. [22], are two constants depending on the overvoltage. By taking for simplicity:

$$a = n\eta^w \quad b = m\eta^w$$

the following relationship is derived:

$$i = n\frac{\eta^{(w+1)}}{u}\exp\left[-m(\eta^{(w+2)}/u^2)\right]$$

This expression presents a maximum which can be computed by setting equal to zero the first derivative of the current intensity as a function of overvoltage. By discarding zero, negative and complex solutions, it can be seen

that the peak current depends on the potential scan rate. For $w = 2$, the peak current is given by:

$$i_p = k\sqrt{u}$$

as expected by the Muller theory [20].

As far as the trend and shape of the voltammetric curves are concerned, it must be noted that the expanders modify both the anodic and the cathodic branches of the voltammetric cycle. This is easily explained because in the former case they affect the structure of the formed sulphate and, in the latter case, they exert an influence on the formation of lead crystals and on hydrogen evolution.

By consideration of the electrochemical reactions which occur during a voltammetric cycle, carried out within a potential range in which the lead oxide is not formed, it can be observed that in the anodic branch of the cycle one single electrochemical reaction occurs. However, in the cathodic branch, hydrogen ion discharge can occur together with lead sulphate reduction. All three processes are influenced by the presence of expanders.

On the basis of the above considerations, it can be noted that, the voltammetric curves provide reliable information about the amount of charge stored in the anodic part of the cycle, i.e., on the formation of sponge lead, while they do not give direct kinetic information about single processes. By plotting the amount of charge of the anodic peak as a function of the cycle number, a curve presenting a wide maximum is obtained [18]. The difference between the maximum value of the amount of charge obtained in the presence of the expander and that obtained without the expander, has been related by the previous authors to the activity of the organic substance, while the difference between the number of cycles for which such maximum values are observed has been correlated to the stability of the expander.

1.2. Potentiostatic transients

In order to investigate the formation and reduction of lead sulphate, a very convenient experimental method is
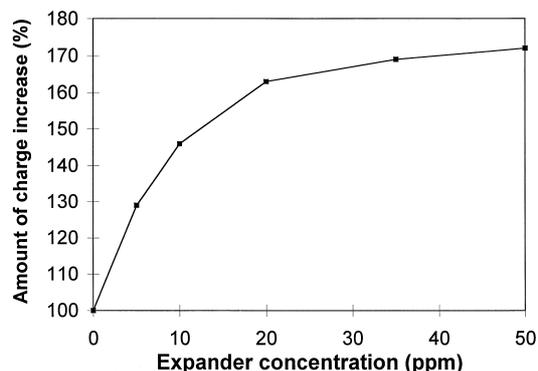
Fig. 4. Percentage increase of the amount of charge of the anodic peak measured at 600 cycles vs. concentration of Vanisperse A in ppm.
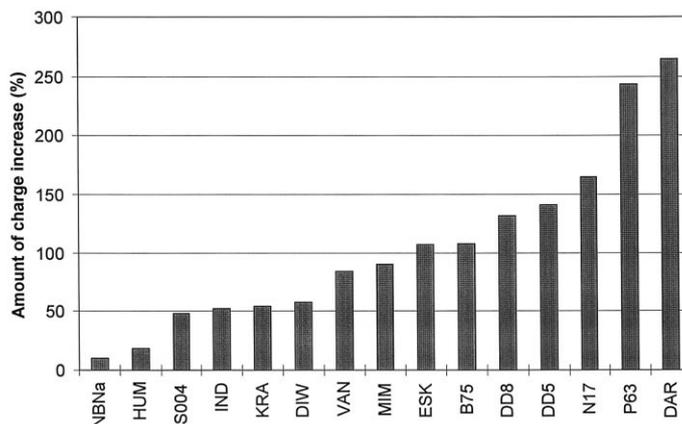
Fig. 5. Percentage increase of the amount of charge of the anodic peak measured at 600 cycles with respect to the voltammogram obtained in pure sulphuric acid for the tested expanders in the concentration of 20 ppm.

the one based on the analysis of potentiostatic transients. This method consists in applying a potential step in the anodic direction to a lead electrode immersed in a sulphuric acid solution, starting from a completely reduced lead surface, and recording the change of the current intensity with time. Similarly, in the case of lead-sulphate reduction, the potential step is applied in the cathodic direction, starting from a potential at which a stable $PbSO_4$ layer has been formed. The interpretation of such transients can be carried out by the well known laws of electrocrystallisation [24] or by a more complex theory proposed by Varela et al. [25,26]. The comparison of the transients obtained in the presence and absence of the expander provides valuable information about the influence of the organic additive on the kinetics of lead-sulphate formation and reduction.

The trend of the transient curves depends on the electrocrystallisation law. If a mechanism based on instantaneous nucleation followed by a two-dimensional growth of the crystals is assumed, the following expression of the transient $i(t)$ curve is derived:

$$i = at \exp(-bt^2)$$

the parameters a and b being defined by:

$$a = 2\, zF\pi hK^2N(M/\rho) \quad b = \pi K^2N(M/\rho)^2$$

where M is the molar mass of lead sulphate, ρ its density, h the film thickness, K is the rate constant, N is the number of nucleation centres, z the number of electrons involved in the electrochemical reaction and F the Faraday constant. The $i(t)$ curve, which presents a maximum value i_{max} for the time t_{max}, can be normalised in the form:

$$\frac{i}{i_{max}} = \frac{t}{t_{max}} \exp\left[0.5 - 0.5(t/t_{max})^2\right]$$

By assuming for lead-sulphate $M = 303$ g mol^{-1}, $\rho = 6.2$ g cm^{-3}, $z = 2$ and expressing the time in seconds, the following relationship is obtained:

$$K\sqrt{N} = \frac{8.16 \times 10^{-3}}{t_{max}}$$

From the transient curves it is possible to determine the value of $K\sqrt{N}$. This factor is inversely proportional to the time t_{max} required to reach the anodic peak current caused by the oxidation potentiostatic step. The ratio between the values of t_{max} measured in the absence and in the presence of expanders provides substantial information about their influence on the kinetics of the anodic process. The higher is t_{max} the more the electrocrystallisation is hampered, due to a lower value of the factor $K\sqrt{N}$. Thus, such ratio can be assumed for evaluating the efficiency of the expanders. It is interesting to note that even if the kinetic law for electrocrystallisation is different from the one assumed (e.g., 2D progressive, 3D progressive, 2D on porous electrodes etc. [24]), the expression $K\sqrt{N}$ is inversely proportional to t_{max}^n with $0.1 < n < 1.5$ so that the previous considerations are still valid.
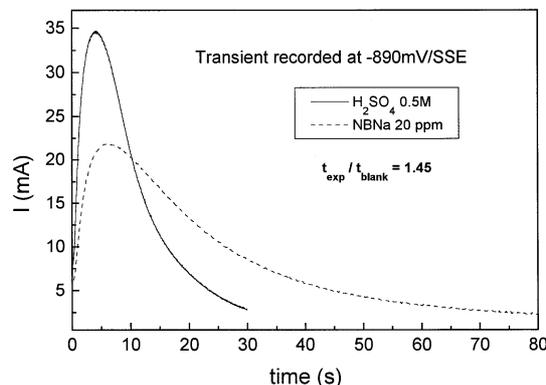
Fig. 6. Oxidation potentiostatic transient recorded at -0.89 V (VS Hg/Hg$_2$SO$_4$ electrode) in 0.5 M sulphuric acid with and without NBNa.
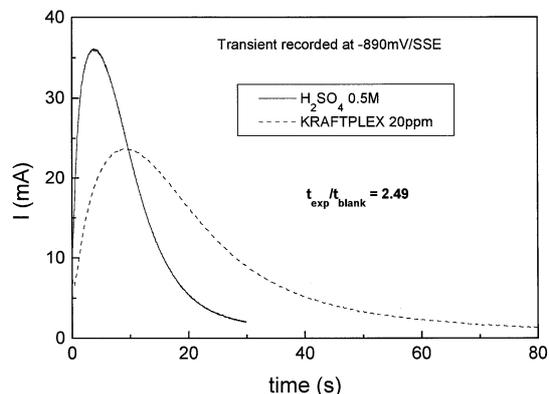
Fig. 7. Oxidation potentiostatic transient recorded at -0.89 V (VS Hg/Hg$_2$ SO$_4$ electrode) in 0.5 M sulphuric acid with and without Kraftplex.

1.3. Impedance measurements

The adsorption of organic substances onto lead can be usefully investigated by means of stationary polarisation curves or by electrochemical impedance. The measurements must be carried out at sufficiently negative potentials where, due to slight hydrogen evolution, no lead-sulphate is present on the electrode surface. Both methods provide similar information because the value of transfer resistance of the hydrogen evolution reaction equals the ratio of the slope of the $V/\log(I)$ curve (Tafel slope) and the stationary value of the current intensity for which the determination of the transfer resistance R_t has been carried out:

$$\frac{dV}{d\log I} = b = R_t I.$$

The frequency range for impedance measurements must be sufficiently wide in order to obtain the accurate values of the transfer resistance and double layer capacitance from the impedance spectra.

2. Experimental

The electrodes, obtained by cutting a pure lead rod (purity 99.9985%), have been embedded in a resin in order to have a flat circular exposed area of about 1 cm^2. At the beginning of each test the working electrode, mechanically polished by emery paper, was cathodically polarised at a constant potential of -1.20 V (VS Hg/Hg$_2$ SO$_4$ electrode), until a steady current in the range of 1 mA was reached, in order to assure a clean lead surface, free of lead sulphate and oxide. The voltammetric and impedance tests were carried out in 1.25 g/cm^3 density sulphuric acid, while the potentiostatic transient tests were performed in 0.5 M sulphuric acid. In all cases the test temperature was 25°C. The addition of expanders to the

sulphuric acid solution was done by previously dissolving the organic substance in the acid solution to be used in the test cell. In order to favour the dissolution process, the lignosulphonate-type additives were first dissolved in a small amount of 0.1 M NaOH, and then added to the electrolyte, whose sulphuric acid content was properly adjusted.

Cyclic voltammetry tests were performed according to the following procedure. A voltage scan range from -1.2 to -0.7 V (VS Hg/Hg$_2$ SO$_4$ electrode) was chosen so that the reactions at the lead electrode were completely developed within these limits, without significant release of hydrogen. The voltage scan rate was 2 mV/s. Cycling was continued until a constant shape of the voltammogram was obtained, this condition is typically achieved after 400 to 800 cycles. If the amount of charge corresponding to the anodic peak area is plotted vs. the number of cycles, it can be observed that such charge steadily increases at the beginning. Then, at about 400 cycles, an almost constant value is reached. If these values are plotted vs. the expander concentration, an increase of the amount of charge with concentration is observed, up to a point where the expander efficiency reaches a plateau, and no significant increase is observed beyond this point. For the majority of the tested expanders, this value is about 20 ppm in the electrolyte.

To study the formation of lead-sulphate by means of potentiostatic transients the lead electrode has been initially maintained at a potential of -1.2 V (VS Hg/Hg$_2$ SO$_4$ electrode) for 30 min to obtain a complete reduction of its surface, then the potential was stepped to -0.89 V (VS Hg/Hg$_2$ SO$_4$ electrode). The duration of this final step, during which recording of the current intensity took place, varied from 10 to 100 s. This procedure was repeated three times, then 20 ppm of the expander were

Table 2
Results of transient oxidation tests at 25°C in 0.5 M sulphuric acid

Expander	t_{exp} / t_{blank}	Effectiveness
DD8	4,48	100
ESK	4,40	98
N17	3,33	74
S004	3,14	70
DD5	3,04	68
DAR	2,78	62
KRA	2,49	56
DIW	2,48	55
B75	2,47	55
P63	2,02	45
VAN	1,84	41
QUE	1,76	39
UP298	1,69	38
HUM	1,61	36
NBNa	1,45	32
IND	1,33	30
MIM	1,09	24
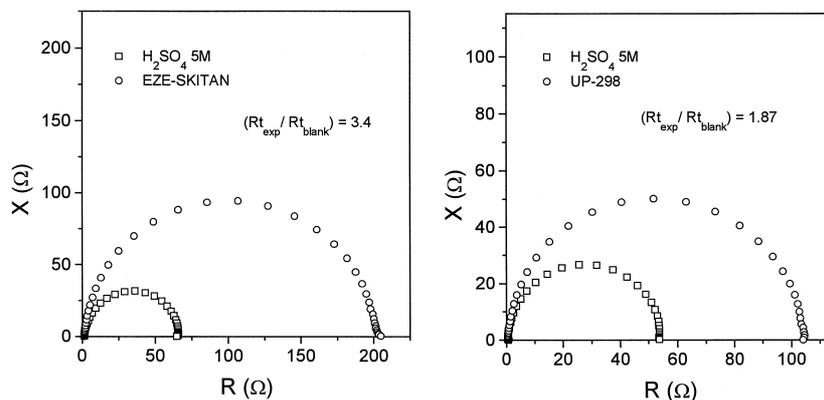
Fig. 8. Impedance data on the Nyquist plot determined in the frequency range 10^4–10^{-2} Hz, in 5 M sulphuric acid with and without the addition of Eze-Skitan (left diagram) and UP-298 (right diagram).

added to the electrolyte and three other similar oxidation/reduction cycles were carried out.

For impedance tests the electrode was first polarised at -1.3 V for a time sufficient to obtain a steady state current (about 20 min), then the impedance spectrum was measured in the frequency range 10^4 Hz e 10^{-2} Hz with an amplitude of the sine signal of 5 mV. Following the first measurement with pure sulphuric acid, a second run was immediately carried out after the addition of the chosen expander to the solution. The Solartron 1150 FRA connected to an AMEL mod. 5011 Potentiostat have been employed.

In the present work a set of seventeen different organic substances has been tested according to the above described techniques. Mostly the examined expanders correspond to commercial materials used in the lead-acid battery industry, in some cases other materials have been selected for their physico-chemical similarity to known expanders.

A list of all tested expanders, together with short information about them, is given in Table 1, where abbreviations used in this work are also shown.

3. Results and discussion

Fig. 1 shows the cyclic voltammetry behaviour of lead in 1.25 g cm^{-3} density sulphuric acid without additives, while Fig. 2 presents the cyclic voltammetry curves obtained when 20 ppm of Vanisperse A were added to the electrolyte. Similar tests have been carried out for different amounts of all the additives, from 5 to 50 ppm. This last value, in some cases, exceeded the solubility limits in the electrolyte.

If the amount of charge corresponding to the anodic peak area is plotted vs. the number of cycles, it can be observed that such charge steadily increases at the beginning, then, at about 400 cycles, an almost constant value is reached, (Fig. 3). Thus, the value of the anodic peak area at 600 cycles has been used for comparing the behaviour of the different expanders.

If the amount of anodic charge at 600 cycles is plotted vs. the expander concentration, such value increases steadily at the beginning of the curve, then, at about 20 ppm for the majority of the tested expanders, reaches a constant value. This behaviour is illustrated in Fig. 4,
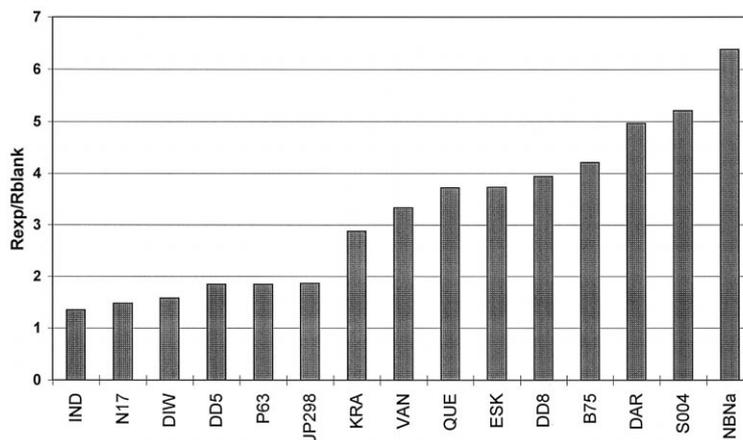
Fig. 9. Transfer resistance ratio R_{exp}/R_{blank} between the value obtained by impedance data in the presence (R_{exp}) and absence (R_{blank}) of the different tested expanders.

Table 3
Effectiveness of the expanders according to the different electrochemical tests

Effectiveness	Cyclic voltammetry	Oxidation transients	Impedance measurements
Major effect	Darvan 1	DD8	NBNa
	P63	EZE-Skitan	S-004
	N17	N-17	Darvan 1
	DD5	S-004	B-75
	DD8	DD5	DD8
		Darvan 1	Mimosa
		Quebracho	Quebracho
Relevant effect	B-75	Vanisperse A	EZE-Skitan
	EZE-Skitan	Kraftplex	Vanisperse A
	Mimosa	P-63	Kraftplex
	Vanisperse A	Humic acid	UP298
	Diwatex	B-75	P-63
	Kraftplex	Diwatex	Humic acid
	Indulin AT	UP298	DD5
Low effect	S-004	Indulin AT	N-17
	Humic acid	NBNa	Indulin AT
	NBNa	Mimosa	Diwatex

where the anodic amount of charge at 600 cycles vs. concentration is plotted in the case of Vanisperse A.

The results obtained with the different organic additives by cyclic voltammetry have been ranked by considering the increase of the amount of anodic charge determined at 600 cycles. Fig. 5 shows the overall results concerning all the expanders tested by this technique.

Figs. 6 and 7 are examples of potentiostatic oxidation transients measured for two expanders of different efficiency. On each diagram both plots, in the presence and in the absence of the expanders are shown. From the ratio t_{exp}/t_{blank} of the t_{max} values measured with and without the organic additive, it is possible to rank the expanders according to their effect. This classification is shown in Table 2, where the values reported under the heading ''effectiveness'' were computed by assigning the arbitrary value of 100 to DD8, the most effective substance with respect to lead sulphate formation; the values for the other expanders were derived accordingly.

Fig. 8 shows the Nyquist plot of impedance data for a lead electrode in absence and in presence of two expanders exhibiting a notably different efficiency. The value of the expression $Ri \log_e 10$, corresponding to the slope of the polarisation curve plotted on a semilogarithmic diagram, was found to be approximately 200 mV, independently of the considered expander. Such value is in good agreement with that obtained by the polarisation curves. In order to compare the effectiveness of the expanders with respect to cathodic polarisation and impedance data, the ratio I/I_{exp} between the steady state value of the cathodic current intensity without expander and in the presence of the expander, and the similar ratio R_{exp}/R between the transfer resistance value measured in the absence and presence

of expanders have been computed. The result of this evaluation is illustrated in Fig. 9.

If the tested expanders are listed according to their effect, resulting from the various electrochemical measurements, the classification shown in Table 3 is obtained, which attempts to rank all the tested substances according to the different electrochemical effects, subdividing the effectiveness in three groups: major, relevant, low.

With reference to Table 3, which summarizes all three electrochemical tests, it is possible to isolate the expanders with the best overall performance by considering the occurrences of each substance in the effectiveness categories.

4. Conclusion

The results of the tests carried out with the various expanders show that all the organic substances examined are adsorbed on metallic lead. In fact the capacitance of the lead-sulphuric acid interphase, measured at potentials below the value of the $Pb/PbSO_4$ couple, markedly decreases in the presence of the expanders.

Adsorption notably affects both the cathodic and anodic electrochemical behaviour of lead in sulphuric acid, namely it affects both hydrogen evolution and lead-sulphate formation.

As far as hydrogen evolution is concerned, impedance measurements showed that the presence of adsorbed organic substances increases hydrogen overvoltage to a higher or lesser extent. In fact it can be observed, at constant potential and with respect to pure sulphuric acid solutions, a marked increase of the transfer resistance R_t, together with a decrease of the steady state cathodic current i, their product remaining almost unchanged.

From such observation about the invariability of the product $R_t\ i = b$ it can be argued that adsorption of the expanders causes a decrease in the extension of the active area on which protons are discharged, thus decreasing the exchange current density $i°$.

As far as the anodic behaviour is concerned, it is known that, for relatively low anodic potentials, lead passivates by forming a layer of lead-sulphate. All literature works related to this subject agree with the interpretation that such layer is constituted by a thin compact film having the properties of a semipermeable membrane on which large crystals, visible at the microscope, grow.

The large lead-sulphate crystals are formed by a dissolution–precipitation mechanism, while the thin compact layer is formed by a solid state mechanism based on instantaneous nucleation followed by a bi-dimensional growth. From the analysis of the oxidation transients it can be seen that expanders slow down, to either a more or less pronounced extent, the solid state process, favouring the dissolution–precipitation mechanism. Thus it can be concluded that for lead oxidised in the presence of expanders the surface area covered by the thin semipermeable layer is lowered.

In conclusion, the results obtained in the present work indicate that the comparison of data provided by different electrochemical techniques such as cyclic voltammetry, potentiostatic transients and impedance measurements can be the basis for defining a reliable method for the selection of the expander materials. This is supported by the observation that cyclic voltammetry, in addition to other important electrochemical aspects, is suitable for characterising the formation of sponge lead on the initial flat surface in the presence and in the absence of the additives, while the transient behaviour for lead-sulphate formation gives specific information on the influence of the additive on the reaction kinetics. In addition, results of impedance measurements, carried out at cathodically polarised lead electrodes, provide important information about the adsorption of the organic additives on lead.

Acknowledgements

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