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Hardening and smoothing effects of lignin sulfonates on the electrodeposition of lead

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The codeposition of lignin derivatives from an acidic lead electrolyte was investigated with respect to the nature of the derivative, the additive concentration in the electrolyte and the current density. The lignosulfonates of sodium and calcium were incorporated in the deposits up to a volume fraction of 1.1–1.2% whereas the codeposition of alkali lignin was much lower. The lignosulfonates were dispersed in the deposit as small inclusions which were distributed very evenly. A significant hardening of the deposited lead, based on both grain refinement and dispersion strengthening by the included organic particles, occurred.

1. Introduction

The electrodeposition of lead is commonly carried out in fluoroborate baths containing a high concentration of lead. Some work has been reported on the use of organic additives to reduce treeing and to obtain smooth deposits, particularly at high current densities [1]. Generally, materials such as gelatine, glue and peptone are employed. Furthermore, some nonionic, cationic or anionic surfactants appear to have produced good plating results. The smoothing efficiency of lignin sulfonic acid and its salts [2, 3], phenolphthalein [2], coumarin [1, 2], eugenol (oil of cloves) [1, 2] and horse-chestnut extract [3] have been investigated. With all these additives used at moderate concentrations a smooth deposition at high current densities has been observed. Wiesner *et al.* [2] have investigated the deposition of lead in the presence of lignin sulfonic acid, coumarin and titanium dioxide. Titanium dioxide and carbon, obviously originating from included organic additives, were determined in the deposits. Hardness and tensile strength of the deposits were found to increase with the carbon content. Information about the quantitative effects of the individual additives was not obtained. The effect of lignin sulfonic acid to harden electrodeposited lead was described [4]. This unequivocal effect could be due to grain refinement of the deposit or to a dispersion hardening in the case of codeposition of fine particles of this additive. Metal matrix composites, where hardening is dominated by the hardness and volume fraction of a second phase rather than by dispersion hardening, have been produced by the electrocodeposition of nickel with TiO_2 or Al_2O_3 [5, 6], of gold with Al_2O_3 [7] and also of lead with dispersoids [8].

A possible mechanism of the codeposition of inorganic dispersoids with a metal was described by Celis, Roos, Buelens and Fransaer [9, 10]. The entire process may be assumed to consist of a sequence of five steps: adsorption of metal ions on the surface of the oxide, convection, diffusion, electrophoresis and adsorption on the cathode surface and codeposition in the deposited metal by reduction of the adsorbed ions. The adsorption of the metal ions on the surface of the dispersoid appears to be the most important step in codeposition. Organic additives can also be codeposited if they form a 'complex' with the metal ions in the electrolyte which diffuses to the cathode. The dependence of the rate of codeposition of the dispersoid on the experimental conditions given in [9] is expected to be similar for the complex of an organic additive with metal ions.

In the present work the electrodeposition of lead in the presence of lignosulfonic acid salts was studied systematically as a function of the nature of the additive, its content in the bath and the current density. Lignosulfonic acid compounds were selected because they are only partly soluble in the electrolyte. They form an adsorption layer on the cathode and a dispersion of varying particle size if added in excess. In this case the lignin adsorbed on the cathode as well as the lignin 'dispersoids' may be included in the lead deposits. For comparison some experiments were done with an alkali lignin. In both cases a hardening effect of the included organic additives was expected. The rate of codeposition of the organic additives with lead was determined by chemical analysis of the deposits formed under different conditions.

Microstructure and hardness of the deposited materials were studied to analyse the effects of the additives.

2. Experimental details

2.1. *Deposition conditions*

In all experiments a standard lead fluoroborate electrolyte containing 130 g dm^{-3} Pb, 100 g dm^{-3} of free acid and 20 g dm^{-3} boric acid was employed. The

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sodium salt (NaLS; Aldrich Chemical Co.) and the calcium salt (CaLS; unknown Italian producer) of the lignosulfonic acid and alkali lignin (Aldrich Chemical Co.) were used as organic additives. These were added to the bath in concentrations of 0.1 to 5% by mass of the lead content (corresponding to 0.13 to 6.5 g dm^{-3}). In the electrolyte the lignosulfonic acid salts are soluble only at concentrations below about 0.6 to 0.8 g dm^{-3}. If the solution was stored for more than 16 h the salts were partially hydrolysed in the highly acidic bath ($pH \le 0$) to free lignosulfonic acid, which is obviously less soluble and therefore forms a dispersion. By adding the salts in excess above the saturation concentration a dispersion was formed at the beginning. For some experiments the pH of the bath was adjusted to 1.5 by neutralizing the excess free acid with ammonium hydroxide. As cathode a cleaned and polished sheet of stainless steel was used. The cathodes were washed with HNO_3 (50%) and chloroform. An active surface of 9 cm^2 was formed by a frame of paraffin film (Parafilm "M", American National Can). Lead anodes (99.99%) of about 15 cm^2 were used to maintain the lead concentration in the bath constant. The current density was varied between 200 and 800 A m^{-2}. Lead sheets of about 0.5 mm thickness were deposited. The entire process was controlled by measuring the cathode and anode potentials during the deposition. A standard Ag/AgCl electrode, connected to the bath by a salt bridge, served as a reference electrode. All experiments were carried out at about 22–23 °C. Usually during deposition the bath was agitated by a magnetic stirrer rotating at 400 rpm.

2.2. *Determination of the codeposition rate of the organic additives*

The amount of organic compounds in the deposited lead was determined from the carbon content measured by the combustion method with an 'RF furnace analyser' (LECO, USA.). In addition, a carrier gas hot extraction method for the determination of oxygen as a component in the lignosulfonates (LS) was used. From these analytical results the volume fraction of the organic molecules in the lead deposits was calculated based on a density of 1.2 g cm^{-3}. In order to determine whether the additives were incorporated as molecules or aggregates in the original size or in the form of electrochemically modified or destroyed molecules the oxygen to carbon ratio in the deposits was analysed. For the preparation of a contamination free sample a chemical etching procedure was used [11]. All organic additives were analyzed for their carbon, oxygen and sulfur content (Table 1).

2.3. *Sample preparation for microstructural examination and mechanical property determination*

The preparation of sections for light microscopy was carried out by polishing with a dispersion based on SiO_2 (OP– U; Struers) after cutting with a diamond saw. To study the microstructural distribution of the codeposited organic material the lead samples (LS content of about 1 vol%) were thinned according to common practice by ion milling and then analysed in a transmission electron microscope CM 20 (Philips). Preparation by an ultramicrotome, which was used for electrodeposited copper with organic inclusions [12], was not a suitable method because of severe damage to the microstructure.

The mechanical properties of the deposited lead sheets were characterized by measurements of the Vickers hardness. A load of 0.196 N was applied for 60 s in order to take the short time creep behaviour of this material into consideration. In each case the measurements were done on the face of the sheet that was in contact with the cathode during the deposition. Thus the influence of the roughness of the sheets could be excluded. The average values were obtained from at least seven single measurements.

The determination of roughness was carried out on the deposit face exposed to the bath. Roughness was measured by laser scanning. For characterizing the roughness the parameter R_a, that is, the arithmetic mean of the absolute values of all profile ordinates along the measuring line, from linescans of 2 mm length was used.

3. Results

3.1. *Surface properties of the deposits*

Macroscopically the roughness of the lead deposits does not differ drastically with the various additives used. Only at the highest current density and the lowest additive concentration was the surface rough and some dendritic growth was observed. In all cases the layer deposited in contact with the cathode surface was smooth. As lead sheets with increasing thickness are deposited their roughness also increases. Figure 1 shows the values of the roughness as a function of the calcium lignin sulfonate content in the

Table 1. Analysis of the lignin derivatives

Compound	*Carbon* /wt %	*Oxygen* /wt %	*Sulfur* /wt %	*Molar ratio* *O/C*	*Molar ratio* *S/C*
Sodium sulfonate	45.9	36.3	5.3	0.592	0.043
Calcium sulfonate	42.7	47.3	4.1	0.833	0.036
Alkali lignin	61.0	19.5	0.07	0.389	

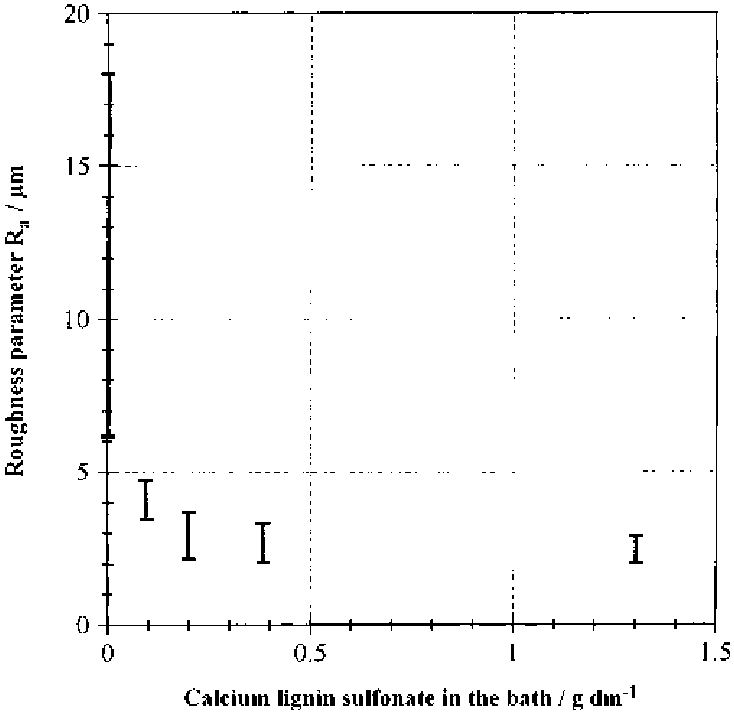

Fig. 1. Roughness of deposited lead versus concentration of calcium lignin sulfonate in the bath. Current density: 600 A m^{-2}. Thickness of the samples: about 0.5 mm.

bath. Deposition without organic additive led to large and irreproducible roughness in all cases. On the other hand an addition of only 0.1 g dm^{-3} of lignin derivative to the electrolytic bath caused a drastic improvement of the surface quality, though some small cones were still found. The decrease in roughness at higher additive concentrations is moderate, but the number of the cones was appreciably reduced. The application of sodium lignosulfonate instead of the calcium salt led to the same smoothing effects. Figure 2 shows the surface quality of a deposit obtained at a concentration of 1.3 g dm^{-3} of calcium lignin sulfonate in the bath.

3.2. *Additive content in the lead deposits*

In Fig. 3 the calculated volume fractions of the organic additives in the deposits are shown as a function of their content in the electrolyte. At lower concentrations of NaLS and CaLS a distinct increase of the additive content in the deposit with increasing additive concentration in the bath was observed. Above an additive concentration of about 1.0–2.0 g dm^{-3} the additive content in the deposit seems to approach a limiting value depending on the nature of the additive. The codeposition rate of alkali lignin is significantly lower at the same concentration than

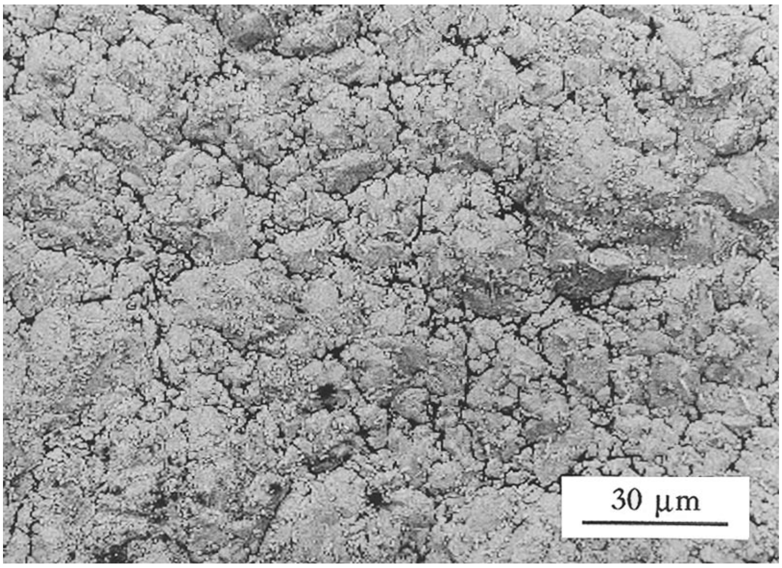

Fig. 2. Surface of deposited lead of a thickness of about 0.5 mm. 1.3 g dm^{-3} calcium lignin sulfonate in the bath. SEM; back scattered electron contrast.

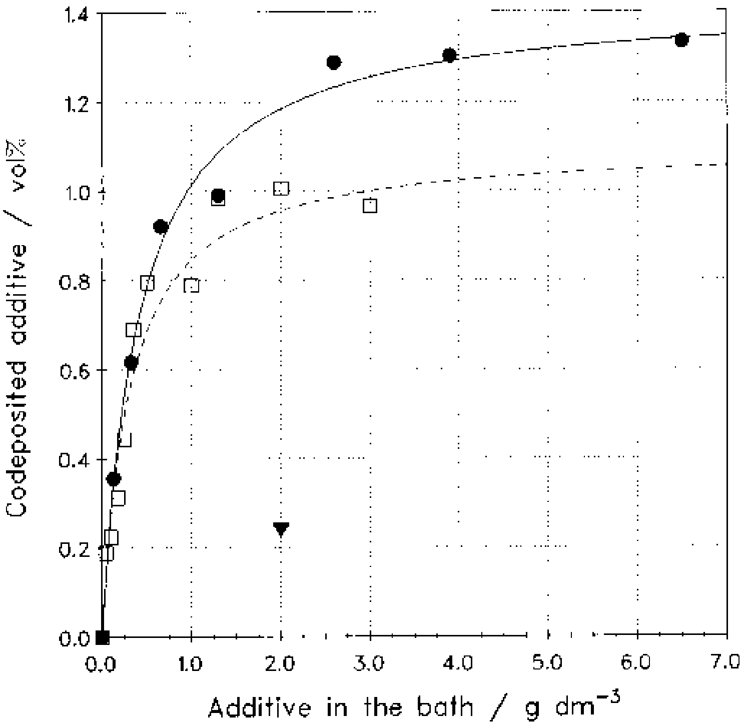

Fig. 3. Codeposition rate of lignin derivatives. Vol % calculated from ρ (Pb) = 11.35 g cm^{-3} and ρ (additive) = 1.2 g cm^{-3}. Current density 600 A m^{-2}. Key: (□) calcium lignin sulfonate; (●) sodium lignin sulfonate; (▼) alkali lignin.

for the lignosulfonic acid salts. In all deposits with NaLS and CaLS, respectively, nearly the same relation between the oxygen and carbon content was found (Fig. 4). The reproducibility is 3–10%. This relationship between oxygen and carbon content is independent of the experimental conditions. This suggests that these additives are incorporated in a molecular form. No distinct influence of either current density or pH (≤ 0–1.5) on the codeposition rate of the lignins was detected.

3.3. *Microstructure of the deposits and evidence for codeposited lignin derivatives*

Figure 5(b) illustrates the influence of lignin sulfonates (0.13 g dm^{-3} NaLS) on the surface morphology

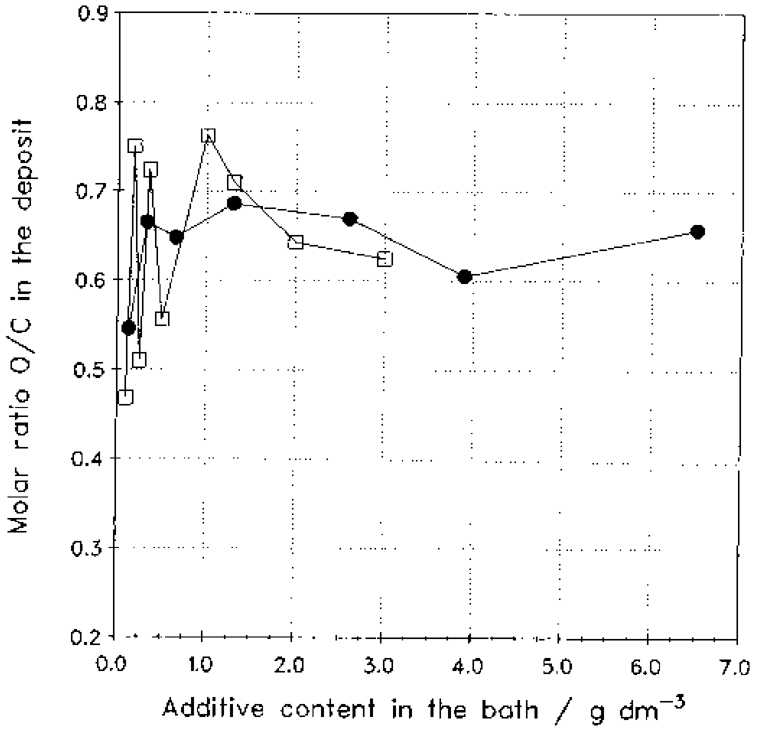

Fig. 4. O/C molar ratio in deposits with lignosulfonic acid salts. Current density: 600 A m^{-2}. Key: (□) calcium lignin sulfonate; (●) sodium lignin sulfonate.

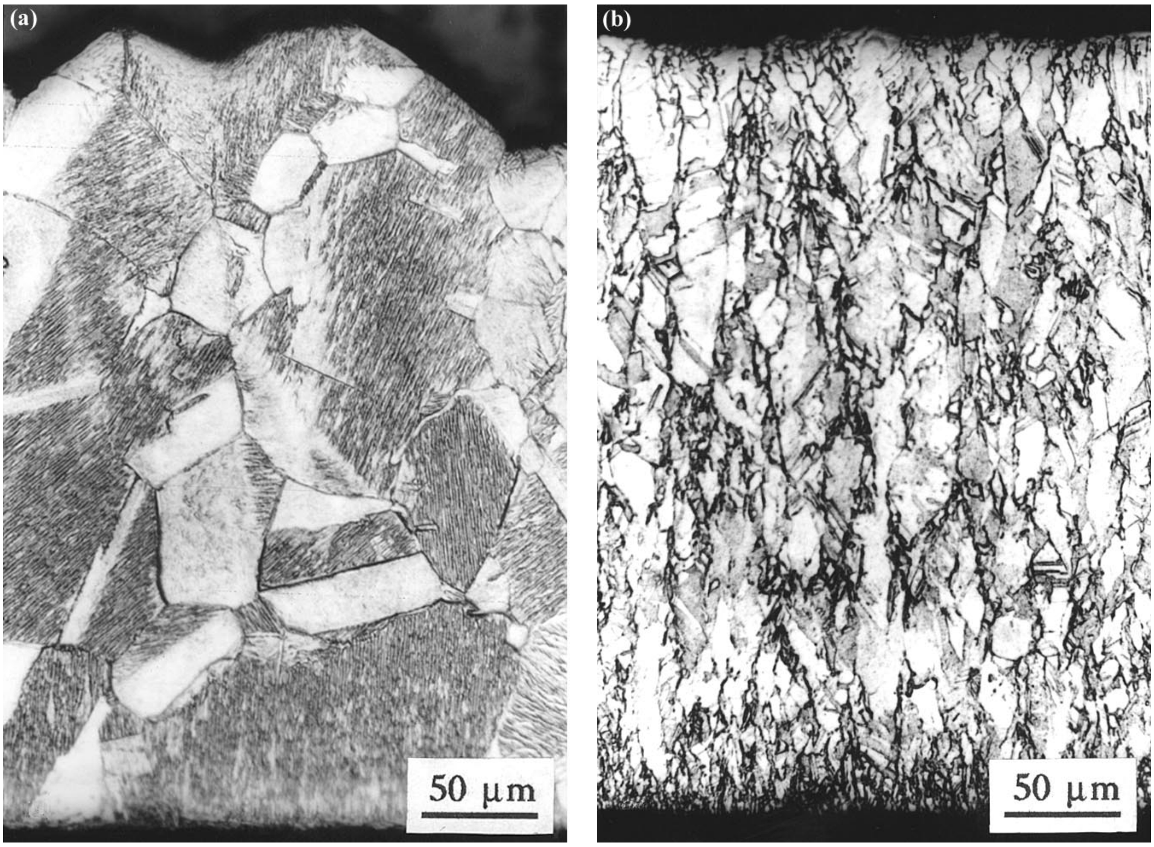

Fig. 5. Cross-section of lead: (a) deposited in a bath with 0.2 g dm^{-3} glue and (b) deposited in a bath with 0.13 g dm^{-3} of sodium lignin sulfonate.

and microstructure of the deposited lead. Apart from the smoothing effect a pronounced grain refinement caused by the inclusion of the macromolecular substances is observed. At variance with the typical cross-section of deposits produced with the addition of glue as smoothing additive (Fig. 5(a)) the grains are extended in the growth direction. At the beginning of deposition, i.e. at the cathode side of the deposit which is shown at the bottom of the micrograph, the grains are isometric and the grain size is below 5 μm. As the thickness of the deposit increases the grains tend to become acicular and their average diameter increases to about 15 μm.

The codeposited lignin sulfonate derivative inclusions were revealed by transmission electron microscopy (Fig. 6). The included organic material appears

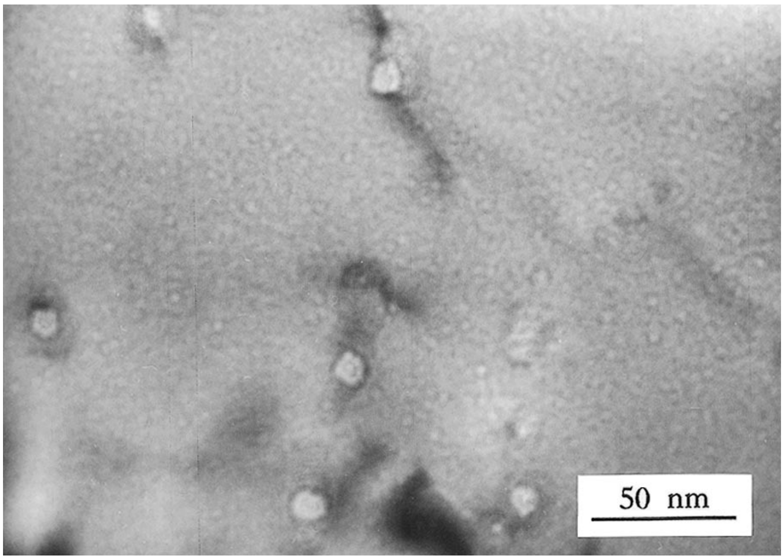

Fig. 6. Typical morphology of the deposited lead with inclusions of lignin derivatives. TEM bright field contrast. Current density during deposition 600 A m^{-2}. Volume content of calcium lignin sulfonate about 1%.

as bright, round structures which show no diffraction contrast because of their noncrystalline character. The organic inclusions are distributed comparatively evenly and their diameter varies from about 5 to 20 nm.

3.4. *Hardness of the deposits*

The addition of calcium and sodium lignin sulfonate to the electrolyte leads to significant hardening of the deposited lead. Figure 7 shows the dependence of Vickers hardness on the volume fraction of the two salts studied. The measured values show a linear dependence; the correlation coefficient for the calcium salt was calculated to be about 0.93. The Vickers hardness of 4.5 HV 0.02/60 represents a typical value for lead samples deposited with 0.2 g dm^{-3} of glue in the bath. With both CaLS and NaLS a hardness of about 10 HV 0.02/60 was reached. Deposition with NaLS after the bath had been pretreated with a high speed dispersing stirrer (1 h at 10 000 rpm), resulted in deposits with a hardness of more than 12 HV. At variance with the effect of the lignin sulfonates the codeposition of alkali lignin has an insignificant effect on hardness.

4. Discussion

Depending on the additive to electrolyte ratio the lignin compounds can persist in the bath as molecules, molecular aggregates or particles of different size. Because of the high acidity of the electrolyte the geometrical shape and size of the lignin molecule could not be determined by the usual methods. A spherical form seems to be the most probable one because of the inter- and intramolecular interaction of hydrogen bonds. Indeed, by means of TEM investigations the codeposited organic particles were localized as more or less globular inclusions, the diameters of which range from 5 to 20 nm. Smaller structures were also observed. However, they could not be distinguished from possible preparation effects. The reasons for this problem are that the codeposited material consists of light elements which are difficult to identify by analysis and that the diffraction contrast is missing. The size of the inclusions show that the lignin sulfonic derivatives were codeposited above all in the form of molecular aggregates. Hope *et al.* [12] also have reported about the incorporation of macromolecular additives which are used in the electrodeposition of copper. Inclusions of polyethylene glycol and polyethylene imine up to 250 nm in size, respectively, and with an irregular shape have been observed by TEM.

According to [9, 10] particles with a compact ion-‘cloud’ can easily be transported to the cathode and included in the structure of the deposit during reduction and crystallization of the ions, partially due to their low diffusion probability away from the cathode surface. The highly active hydroxyl and methoxyl groups of the lignin molecule, as well as the sulfonate groups in the lignosulfonates, cause adsorption of ions, i.e. protons and Pb^{2+}, on the surface of molecules as well as of the molecular aggregates. In the case of lignin sulfonates even the formation of complexes with Pb^{2+} is possible. Therefore, molecules

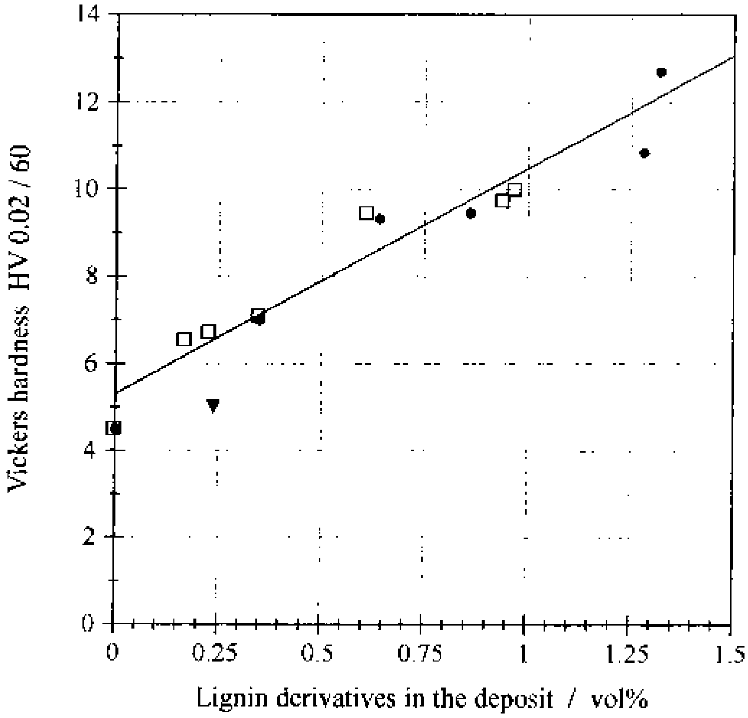

Fig. 7. Vickers hardness as a function of the content of codeposited lignin derivative. Average values of at least seven single measurements on the cathodic side of the deposited sheets. Additive in electrolyte: (□) calcium lignin sulfonate; (●) sodium lignin sulfonate; (▼) alkali lignin.

or particles of different lignin additives can also be codeposited at a different rate according to their adsorption activity, surface charge and diffusivity. The small difference between the codeposition rates for the sodium and calcium lignin sulfonates (Fig. 3) could be explained by the different content of sulfonic groups (in accordance with the data in Table 1). The lower codeposition rate of the alkali lignin seems to be caused by the lower degree of adsorption of Pb^{2+} on it. Its distinct smoothing effect shows that it is adsorbed predominantly on the growing cathode surface and acts as an inhibitor. Using the lignosulfonates both the smoothness and the codeposition rate were increased. Comparing the influence of experimental conditions on the deposition of inert dispersoids described in [9, 10] with our results some differences are evident. In the range between 200 to 800 A m^{-2} no systematic influence of the current density on the rate of codeposition could be found for any of the lignin derivatives. The codeposition is influenced by the bath movement only at low rates, it increases with the speed of rotation of about 300 rpm; above 400 rpm it remains independent. The increase of pH from initially 0.1...0.3 to 1.5 does not affect the rate of codeposition beyond the scatter of the carbon determination. Whereas, in accordance with [9, 10], the rate of codeposition increases with the concentration of the lignins in the bath and reaches a limit at about 1–1.5 g dm^{-3}. The difference of the influence of experimental conditions on the codeposition of lignin sulfonates and inorganic dispersoids, described by Celis *et al.*, is probably caused by the difference in adsorption of Pb-ions and adsorption behaviour on the cathode surface as well as the range of parameters selected for the electrodeposition. Comparing our results of codeposition of lignin sulfonates with those of codeposition of titanium dioxide studied by Wiesner *et al.* [2] it is obvious that lignosulfonic acid derivatives are much more prone to codeposition than the inert oxide dispersoids. Even at low concentrations of the lignin derivatives in the bath a relatively high rate of codeposition can be reached. These results clearly indicate that the influence of the deposition parameters on the codeposition rate must be specified in each case.

The codeposition of both lignin sulfonates leads to a distinct increase in hardness. At only 1 to 1.2 vol % of lignin sulfonate in the deposit its hardness is higher by a factor of 2. The effect of the lignin 'dispersoids' could be slightly improved by deaggregation of the particles in the bath, and, thus, in the deposit. From microstructural observations it is obvious that the hardening observed is based on both grain refinement and dispersion strengthening by the included organic particles. More quantitative conclusions about the relative influence of these effects will be drawn on the basis of further investigations, taking into account also the possible influence of internal stresses.

In [2] a hardening effect of lead deposits due to the application of lignin sulfonic acid, coumarin and titanium dioxide in a similar electrolyte was mentioned as a common feature. An increase in the strength of the electroformed lead depending on carbon content was stated. However, no quantitative function of any of the bath components was determined. Comparing these results with our observations we may conclude that the hardening can be caused by lignosulfonic acid and its salts alone with a strong linear correlation between the content of the additive and the Vickers hardness. A comparison of the hardness of deposits containing lignin sulfonic and alkali lignin derivatives, respectively, shows that at the same volume content the efficacy of the two lignin sulfonic salts is significantly higher.

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