

Short communication

# Fundamental study of effect of quinone structures in the lignin preparations on negative electrode of lead-acid battery

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## Abstract

The influence of quinone structures related to the formation of the “colloidal deposit” on Pb electrode immersed into water containing lignin preparations or pure organic compounds has been investigated. It was found that quinone structures in lignin preparations, as well as in pure organic compounds, play an important role in the formation of the “colloidal deposit”.

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## 1. Introduction

Lignin preparations, such as lignosulfonates, are organic matters recovered from an effluent of a sulfite pulping process. When added to negative pastes of lead-acid batteries, they have physical, chemical and electrochemical effects on the negative active materials (NAM) [1]. It is well known that they influence the fluidity and the plasticity of the negative paste; they regulate the ratio of different kinds of lead sulfate crystals (3BS, 4BS, etc.) during mixing and curing; they also directly affect the battery performances [2–12]. The expander action of the functional groups in the lignin preparations has also been investigated by many researchers [13–19]. However, it is not yet completely understood, mainly because the lignin preparations perform many tasks in the negative electrode of lead-acid battery [19].

The negative pastes of the battery are usually based on leady oxide and additions of lignin preparations, barium sulfate, carbon black, and so on. In our previous paper [20], it has been found that immersion of Pb plate covered by native oxide (as a model of leady oxide) into water containing partially desulfonated lignosulfonate (Vanillex N, Nippon Paper Chemicals Co., Ltd.) for

24 h resulted in the formation of “colloidal deposit” on the Pb plate, as shown in Fig. 1. Recently, we have also demonstrated that the formation of the “colloidal deposit” on the Pb electrode surface leads to the deposition of the larger lead sulfate crystal during anodic oxidation (=during discharging) and the slower dissolution of the lead sulfate crystals during cathodic reduction (=during charging) in sulfuric acid solution [21]. The importance of the “colloidal deposit” covering the leady oxide surface to the NAM structure has been already pointed out by Száva [8] and von Borstel et al. [14]. However, the effect of the functional groups in the lignin preparations on the formation of the “colloidal deposit” is still obscure.

In this paper, we investigated the influence of quinone structures in lignin preparations upon the formation of the “colloidal deposit” on Pb electrode immersed into water containing lignin preparations.

## 2. Experimental

### 2.1. Lignin preparations and pure organic compounds

In the present work, different types of lignin preparations, such as LS (sodium salt of lignosulfonic acid (Ardrich, No. 47103-8)) and DLS (sodium salt of partially desulfonated lignosulfonic acid (Ardrich, No. 47106-6)) have been used.

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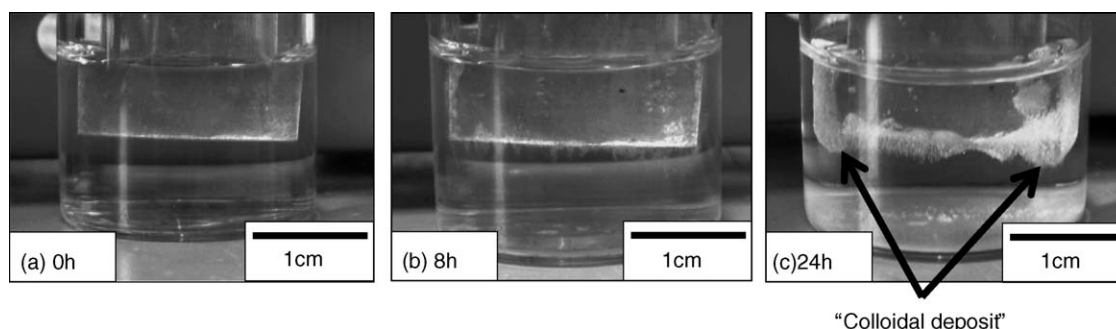


Fig. 1. Formation of the “colloidal deposit” on a Pb plate, which was immersed into water containing Vanillex N. (a) Immediately after immersion of a Pb plate; (b) 8 h after (a); (c) 24 h after (a).

In addition, the lignin preparations actually used in lead-acid batteries, such as Vanillex N, Vanispeare A (Borre-gaard Ligno Tech), Kraftplex (West Vaco), Indulin AT (West Vaco), REAX85A (West Vaco), REAX88B (West Vaco), were also used in the experiments. The pure organic compounds used here are: 1,2-naphthoquinone-4-sulfonic acid sodium salt (Kanto Kasei), anthraquinone-1-sulfonic acid sodium salt (Kanto Kasei), anthraquinone-2-sulfonic acid sodium salt (Kanto Kasei), anthraquinone-2,6-disulfonic acid disodium salt (Kanto Kasei), 1-aminoanthraquinone (Kanto Kasei), 1,5-diamino-anthraquinone (Kanto Kasei), 1-naphthalenesulfonic acid sodium salt (Kanto Kasei), 1-naphthol-4-sulfonic acid sodium salt (Wako), 1-naphthol-8-sulfonic acid sodium salt (Wako), 2-naphthol-6-sulfonic acid sodium salt (Wako), 2,3-dihydroxynaphthalene-6-sulfonic acid sodium salt (Wako), and vanillin (Kanto Chemical).

## 2.2. Measurement of ultraviolet (UV) spectra

Ultraviolet (UV) spectra of aqueous solutions containing the lignin preparations have been measured. In this experiment, two kinds of the aqueous solutions were used. The first one was the alkaline solution (pH 12.2) consisting of 0.2 ml of solution A (0.053 g of the lignin preparations + 100 ml of 50 mM  $\text{H}_3\text{PO}_4$  solution) and 2.8 ml of 100 mM NaOH solution. The second one was the acid solution (pH 2.2) with 0.2 ml of solution A and 2.8 ml of 50 mM  $\text{H}_3\text{PO}_4$  solution.

## 2.3. Dipping experiment

The Pb plates, prepared as follows, were dipped into the water containing 100 ppm of the lignin preparations obtained from ultra pure water ( $>18 \text{ M}\Omega \text{ cm}$  in the electric resistance, Simpli Lab-UV) and the lignin preparations. The Pb plates were as-received without pretreatment and the surface of the samples was covered by the native oxide. The sample preparation of the Pb plates was almost the same as that reported previously [20].

## 2.4. Mixing experiment

Two kinds of solutions were mixed in this experiment. One was 200 ml of water containing 100 ppm of the lignin prepara-

tions or 2.5 mM pure organic compound, which was prepared from ultra pure water, the lignin preparations or the pure organic compounds. The other was 200 ml of almost saturated lead salt aqueous solution, which was prepared from ultra pure water and lead salts. The lead salts used here were  $\text{Pb}(\text{NO}_3)_2$  (Wako),  $\text{PbCl}_2$  (Wako),  $\text{Pb}(\text{ClO}_4)_2$  (Wako), and  $(\text{CH}_3\text{COO})_2\text{Pb}$  (Wako).

## 2.5. Estimation of sulfur content

Total sulfur contents were estimated by the Schniger combustion method [22] using a FHO-A type oxygen combustion flask (Hamada Rika Co., Japan). The released sulfuric acid from the combustion of either LS or DLS was determined with an ion chromatogram equipped with a SI90-4E column (Shodex, Japan). The estimation of inorganic sulfur contents was carried out by the determination of sulfuric and sulfonic acid anions in LS or DLS solution. The dissolved anions were measured by the ion chromatogram mentioned above. Organic sulfur contents of LS or DLS were calculated as a difference between the total and the inorganic sulfur contents determined before.

## 3. Results and discussion

### 3.1. Quinone structures in lignin preparations

Ritchie [13] has investigated the effects produced by the addition of more than 30 kinds of pure organic compounds on the NAM of lead-acid battery. He has found that some of the quinones, such as benzoquinone, naphthoquinone, anthraquinone, have expander properties. However, some of the lignin preparations also have quinone structures. Fig. 2 shows UV spectra of water containing LS or DLS. As negative paste during the mixing is alkaline [1], the UV spectra of the alkaline solution have been used for a comparison. It is found that the UV spectrum of the alkaline solution containing LS had absorption maxima only at less than 300 nm, while that of the solution containing DLS had absorption maximum at 340 nm, as well as those at less than 300 nm. The absorption maximum at 340 nm is known to be caused by quinone structures in the lignin preparations [23], so that DLS contains much more amount of quinone structures than LS. It was also found that the UV spectra of the lignin preparations actually used in lead-acid batteries, such as

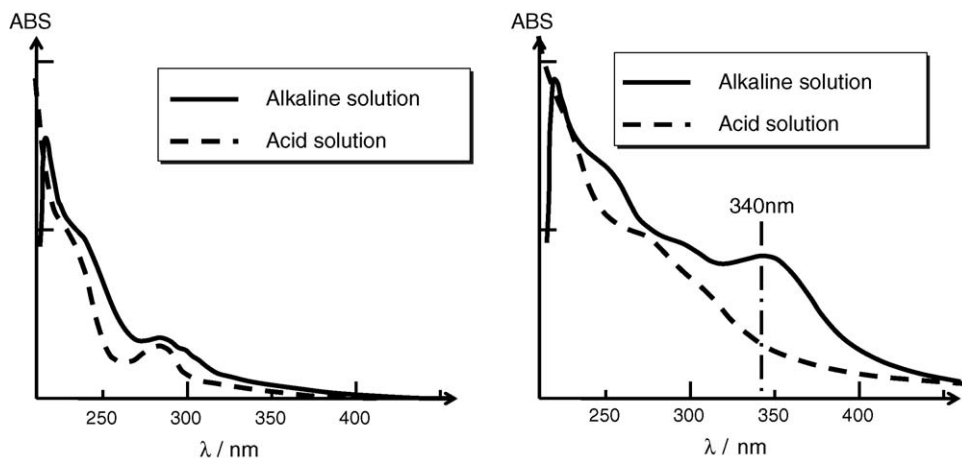


Fig. 2. Ultraviolet (UV) spectra of (a) LS or (b) DLS in alkaline solution or acid solution. Alkaline solution: 0.2 ml of solution A + 2.8 ml of 100 mM NaOH solution (pH 12.2); acid solution: 0.2 ml of solution A + 2.8 ml of 50 mM  $\text{H}_3\text{PO}_4$  solution (pH 2.2); solution A: 0.053 g of LS or DLS + 100 ml of 50 mM  $\text{H}_3\text{PO}_4$  solution.

Vanillex N, Vanispeare A, Kraftplex, Indulin AT, REAX85A, REAX88B, also had absorption maximum at 340 nm indicating that these lignin preparations also had quinone structures.

### 3.2. Dipping experiment

The photos of Pb plates 24 h after the immersion into water containing 100 ppm of LS or DLS are shown in Fig. 3. No deposit was observed on the Pb plate immersed into the water containing LS, while the “colloidal deposit” was formed on the plate immersed into the water containing DLS.

### 3.3. Mixing experiment

The photos of the beakers filled with the mixed water of the aqueous solution containing 100 ppm of LS or DLS and

1.6 M  $\text{Pb}(\text{NO}_3)_2$  aqueous solution are shown in Fig. 4. These pictures were obtained 24 h after the mixing. No deposits were observed in the former beaker, while colloidal deposit was formed on the bottom of the latter beaker. Colloidal deposit was also formed 24 h after mixing of water containing 100 ppm of DLS with almost saturated  $\text{PbCl}_2$ ,  $\text{Pb}(\text{ClO}_4)_2$ , or  $(\text{CH}_3\text{COO})_2\text{Pb}$  aqueous solution. Colloidal deposit was also formed 24 h after mixing of water containing 100 ppm of Vanillex N, Vanispeare A, Kraftplex, REAX85A, or REAX88B with 1.6 M  $\text{Pb}(\text{NO}_3)_2$  aqueous solution. It is noteworthy that volume of colloidal deposit in the “mixing experiment” looks larger, but the peak height at 340 nm of UV spectra in alkaline solution containing lignin preparations (DLS, Vanillex N, Vanispeare A, Kraftplex, REAX85A, REAX88B, etc.) is higher. Within our experiments, when the deposit was formed in the “dipping experiment”, the deposit was also formed in the “mixing experiment”.

### 3.4. Organic sulfur content in the LS or DLS

In order to get a knowledge of the relationship between the “colloidal deposit” formation and the content of organic sulfonic acid groups in the lignin preparations, the organic sulfur content

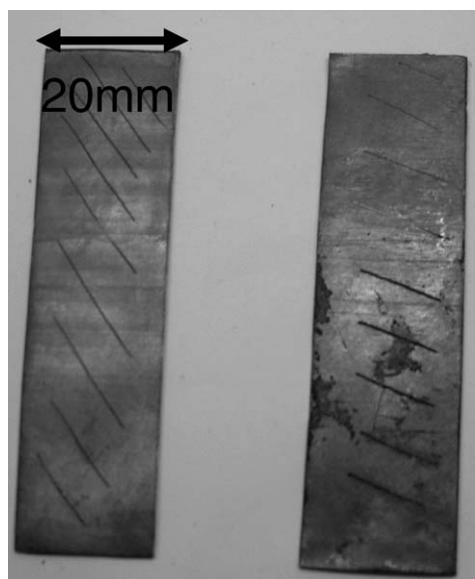


Fig. 3. Pb plates immersed into water containing 100 ppm of LS or DLS for 24 h.

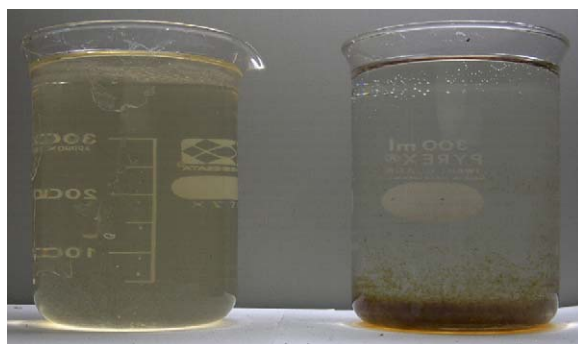


Fig. 4. “Mixing experiment” of water containing LS or DLS and 1.6 M  $\text{Pb}(\text{NO}_3)_2$  solution.

Table 1  
Sulfur content in LS and DLS

	Total S ( $\mu\text{M g}^{-1}$ )	Inorganic S ( $\mu\text{M g}^{-1}$ )	Organic S ( $\mu\text{M g}^{-1}$ )
LS	197.71	20.920	176.79
DLS	83.89	12.808	71.08

Table 2  
Results of “mixing experiment” for water containing 2.5 mM pure organic compound and 1.6 M  $\text{Pb}(\text{NO}_3)_2$  aqueous solution

Colloidal deposit formation	No deposit
1,2-Naphthoquinone-4-sulfonic acid sodium salt	1-Naphthalenesulfonic acid sodium salt
Anthraquinone-1-sulfonic acid sodium salt	1-Naphthol-4-sulfonic acid sodium salt
Anthraquinone-2-sulfonic acid sodium salt	1-Naphthol-8-sulfonic acid sodium salt
Anthraquinone-2,6-disulfonic acid disodium salt	2-Naphthol-6-sulfonic acid sodium salt
1-Aminoanthraquinone	2,3-Dihydroxynaphthalene-6-sulfonic acid sodium salt
1,5-Diaminoanthraquinone	Vanillin

in LS and DLS has been estimated. Table 1 shows the total, inorganic and organic sulfur content in LS and DLS. The organic sulfur content was obtained from the comparison between total and inorganic sulfur content. The organic sulfur content in LS is only two to three times higher than that in DLS (Table 1). The origin of organic S is known to be mainly from organic sulfonic acid groups and partly from other organically bound sulfur. These results suggest that organic sulfonic acid groups do not play an important role in the formation of the “colloidal deposit”. However, to elucidate the relationships between the formation of the “colloidal deposit” and the organic sulfonic acid groups in the lignin preparations, new experiments are necessary.

### 3.5. Mixing experiment of water containing pure organic compounds and almost saturated $\text{Pb}(\text{NO}_3)_2$ solution

Table 2 shows results of “mixing experiment” for water containing 2.5 mM pure organic compound and 1.6 M  $\text{Pb}(\text{NO}_3)_2$  aqueous solution. It was found that colloidal deposit was formed when the pure organic compounds had quinone structures, while no deposit was formed when the pure organic compounds had no quinone structures. These results indicate that quinone structures in the lignin preparations, as well as in the pure organic compounds, play an important role in the formation of the “colloidal deposit”.

## 4. Conclusions

We have investigated the influence of quinone structures in lignin preparations upon the formation of the “colloidal deposit” in the “dipping experiment” and in the “mixing experiment”. The conclusions are as follows:

1. The UV spectra of the aqueous solution containing LS or DLS show that DLS contains higher amount of quinone structures than LS.
2. When a Pb plate, whose surface was covered by native oxide, was immersed into water containing 100 ppm of LS or DLS for more than 24 h, no deposits were observed on the Pb plate immersed into the water containing LS, while the “colloidal deposit” was formed on the plate immersed into the water containing DLS.
3. No deposit was formed 24 h after mixing of water containing 100 ppm of LS with almost saturated  $\text{Pb}(\text{NO}_3)_2$  ( $\text{PbCl}_2$ ,  $\text{Pb}(\text{ClO}_4)_2$ , or  $(\text{CH}_3\text{COO})_2\text{Pb}$ ) solution. On the contrary, colloidal deposit was formed 24 h after mixing of water containing 100 ppm of DLS with almost saturated  $\text{Pb}(\text{NO}_3)_2$  ( $\text{PbCl}_2$ ,  $\text{Pb}(\text{ClO}_4)_2$ , or  $(\text{CH}_3\text{COO})_2\text{Pb}$ ) solution.
4. Colloidal deposit was formed 24 h after mixing of water containing 2.5 mM pure organic compound having quinone structures with 1.6 M  $\text{Pb}(\text{NO}_3)_2$  solution. On the other hand, no deposit was formed 24 h after mixing of water containing 2.5 mM pure organic compound without quinone structures with 1.6 M  $\text{Pb}(\text{NO}_3)_2$  solution were mixed

These conclusions indicate that quinone structures in lignin preparations, as well as in the pure organic compounds, play an important role in the formation of the “colloidal deposit”.

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