

Characterization of some organic additives and their effect on the anodic dissolution of lead

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Certain organic substances are commonly added to the negative (lead) electrode of the lead-acid battery to improve its capacity. Five commercial additives and a dye were characterized using several analytical and electro-chemical methods. Elemental analyses showed that the additives consisted of 10-11 carbon atoms and 10-13 hydrogen atoms. Thin-layer and reverse-phase high-pressure liquid chromatography indicated that the additives were large polar substances consisting of three to six components present in different amounts.

The stability of the additives in sulfuric acid solutions was studied by ultraviolet-visible and infrared spectroscopy. Infrared spectra, in particular, demonstrated structural changes in the nature of the additives after prolonged standing in sulfuric acid.

Linear scan voltammetry and chronopotentiometry on smooth lead-foil electrode support the dissolution-precipitation mechanism during the anodic dissolution of lead in the presence of additives. The additives apparently prevent the formation of a passivating film of lead sulfate at the lead electrode. With prolonged standing in acid, the additives lost their effect on the lead electrode and the solid-state mechanism prevailed. Voltametric titration of the additives with lead (II) ions suggested that the additive may bind with lead (II), possibly through a complexation reaction.

Key Words: organic additives; battery expanders; lead-acid battery; lead anodic dissolution; lead electrode

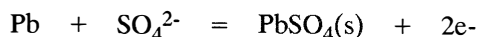
The industrial processes by which the lead (negative) electrodes of lead-acid batteries are produced are usually specific for each manufacturer. In essence, the process consists of reducing a mixture of lead oxide, hydroxide, sulfate, and lead in dilute sulfuric acid. In addition, three materials are normally incorporated: carbon black, barium sulfate, and approximately 0.3% of an organic additive (originally referred to as "expander" because of its apparent physical effect on the lead electrode). Carbon black is added to increase the conductivity of the electrodes and has no electrochemical effect on the performance of the battery. The role of barium sulfate is not clearly understood; Hampson and Lakeman (1) suggested that it provides nucleation centers for lead sulfate. The organic additives are believed to improve the capacity (or total amount of charge obtainable from the battery), which is usually controlled by the negative electrode (2).

Many different wood derivatives and paper mill dust have been added to the negative plate since it became evident that the wooden separator of the early version of the lead-acid battery somehow imparted greater capacity to the battery (3). At present, the additives commonly used commercially are derivatives of natural products such as lignins and lignosulfonic acids; however, synthetic and natural tanning agents may also be used (4).

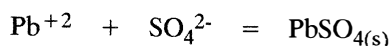
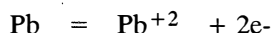
The structure of these additives is not definitely established. It is believed that the molecular structure of the product is influenced both by the raw material and process variables and the nature of the cations present in the molecule (3).

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The mechanism by which the additive exerts its beneficial effect has been the subject of several studies, but there does not appear to be complete agreement on the mode of action at the present time. Archdale and Harrison (5,6) observed that lead dissolves in sulfuric acid at low anodic potentials to Pb^{2+} ions and lead sulfate ions $(\text{Pb}(\text{SO}_4)_2)^{2-}$, and at more anodic potentials (measured at 0.307 V vs. hydrogen electrode) to solid PbSO_4 . Two possible mechanisms for the formation of PbSO_4 were proposed: the solid-state mechanism, i.e.,



and the dissolution-precipitation mechanism, i.e.,



Subsequent work (7,8) further suggested that the soluble species is formed reversibly and the rate of dissolution depended strongly on the anion concentration.

Brennan and Hampson (9), working on smooth lead electrodes, demonstrated that the addition of additives to the electrolyte generally resulted in an increase in the charge necessary to effect passivation. The additive, therefore, acts as a passivation inhibitor. The same workers later inferred from the potentiostatic pulse measurements that the effect of the organic additive was to suppress the encapsulation of PbSO_4 by Pb in the initial stages of charging (10). Hampson and Lakeman (11,12) also compared the behavior of smooth and porous lead electrodes during both oxidation of lead to lead sulfate and the reverse (reduction) process.

The nature and stability of the additives in the course of several discharge-charge cycles has been hardly described. This is probably due to the undefined structure and heterogeneous nature of the additives, the multitude of variables involved in the preparation of the lead electrode, and the lack of convenient analytical methods for characterizing these additives in the system.

This study has sought: (i) to characterize some commercial expanders by several analytical techniques; (ii) to determine their stability in sulfuric acid; and (iii) to reduce their role in the anodic dissolution of lead.

Materials and methods

Reagents

Five commercial additives ("expanders,") provided by Varta Batteries (Frankfurt, Federal Republic of Germany): Bulgarian lignin (BL), calcium ligninsulfonate (CL), indulin (IN), sodium oxylignin (SO), sodium huminate (SH); a dye, sodium alizarinsulfonate (SA; Merck Chemicals), was also used. Analytical reagent-grade (Merck Chemicals) sulfuric acid, nitric acid, organic solvents, lead nitrate, and mercuric nitrate monohydrate were used. All solutions were prepared with doubly-distilled deionized water.

Characterization of the Additives

Elemental Analysis. Carbon, hydrogen, and nitrogen content were analyzed using a Perkin-Elmer model 240 C analyzer.

Spectroscopic measurements. Ultraviolet-visible absorption spectra of various solutions of the additives in different concentrations of sulfuric acid were recorded using Shimadzu Multipurpose UV Spectrometer Model 50L. Stability studies also employed a Perkin-Elmer Model 551 UV-Visible spectrophotometer.

Since the solubilities of the additives were not known and were quite difficult to measure, saturated solutions of the additives in sulfuric acid were prepared. The concentrations of the solutions of the additives were then expressed in terms of the dilution of the filtered saturated solution in the various acid solutions; e.g. 3.0 S/100 means 3.0 mL of the saturated solution was diluted to 100.0 mL.

Two sets of stock saturated solutions of each additive and dye in 1.0 M H_2SO_4 were prepared: one set was kept saturated with respect to the additive for the duration of the study; the other set was filtered after standing for 24 hours. At intervals of 5-12 days, diluted solutions of the additives were prepared from the stock solutions and absorption spectra were taken.

Infrared spectra (Perkin-Elmer Infracord Spectrophotometer Model 137B) of the additives (all pelletized with KBr) were taken using (i) 0.5 mg of each of the additives; and (ii) dried residues recovered from the saturated solutions of the additives.

Thin-layer chromatography. A separation of the components of each additive by thin-layer chromatography was attempted. The supernatant of 0.10% (w/v) saturated aqueous solutions of calcium ligninsulfonate, indulin, and sodium huminate were chromatographed using alumina TLC plates coated with fluorescent indicator and several solvent systems (methanol-ethyl ether, ethyl acetate-methanol, ethyl acetate-ethyl ether, isopropyl alcohol-ethyl acetate, CCl_4 -ethyl acetate and CCl_4 -methanol) mixed in various proportions (13).

High-performance liquid chromatography. Five microliters of the filtrate of 0.1% (w/v) solutions of the additives in methanol were chromatographed using a Waters Associates Solvent Delivery System Model 6000A liquid chromatograph, coupled with a Waters Associates Model 440 UV absorbance detector set at the wavelength 280 nm, a reverse-phase Waters Associates $\mu\text{Bondapak C18}$ column, and an Omniscribe chart recorder. Methanol and 4:1 (v/v) mixture of methanol and 60% acetic were used as mobile phases at a flow rate of 0.70 ml/min.

Electrochemical Studies

Lead electrode. Pure lead foil (one-nm thick, Alfa Products, Danvers, MA, USA) soldered to a platinum wire and sealed in soft glass; a copper wire connected the electrode to the external circuit.

The electrode was pretreated by chemical etching for a few minutes in a saturated solution of ammonium oxalate until the electrode surface appeared shiny.

Glassy carbon electrode. A glassy carbon electrode (GCE) was constructed by cementing a three-millimeter diameter glassy carbon disk (Ringsdorf-Werke, Bonn, Federal Republic of Germany) with epoxy resin into a glass tubing. Mercury in the glass tubing made electrical contact with the glassy carbon and a copper wire was dipped into the mercury for external connection.

The GCE was mechanically pretreated prior to use by polishing on felt cloth in an aqueous suspension of Al_2O_3 (0.3 micron) until the surface of the disk exhibited a mirror finish.

A mercury-filmed GCE was used in the voltammetric titration of additives. It was prepared by electrodeposition of mercury at -0.70 V (versus a saturated calomel electrode) for one minute in a stirred, deaerated 50.0-mL 0.010 M $\text{Hg}(\text{NO}_3)_2$ solution.

Reference and auxiliary electrodes. A commercial probe-type saturated calomel electrode (SCE) used was the reference electrode. The auxiliary electrode was a five-mm long platinum wire sealed in soft glass.

Electrochemical equipment. The voltammetric equipment was a modular set-up consisting of a Gerhard Bank Elektronik potentiostat (Wenking Model LB75L) coupled with a voltage scan generator (Wenking Model VSG 72) and a Rhode and Schwarz ZSK-2 XY recorder.

Chronopotentiometric studies employed a circuit constructed from operational amplifiers (13). It involved a constant current source (2.8 or 7.1 microamperes) and a voltage follower which measured the difference in potential between the lead electrode and the reference electrode.

Linear scan voltammetry. This technique was used to follow the anodic dissolution behavior of lead in different concentrations of sulfuric acid and of additives, and in additive solutions of different periods of storage.

Voltammetric titration of additives with lead (II). A 100-mL aliquot of 0.10% (w/v) or saturated solution of each additive in 0.10 M HNO₃ was titrated with 100 ppm lead(II) nitrate solution, using volume increments of 0.05 mL for the first 0.50 mL, and 0.10 mL for the next 0.50 mL of titrant. The lead(II) ions were allowed to react with the additives for two minutes with constant stirring. Unreacted lead(II) ions were then analyzed by anodic stripping voltammetry: Pb(0) was pre-concentrated on a mercury-filmed-GCE by electrodeposition for ten minutes at -0.80 V (versus SCE) and the voltage was subsequently scanned from -1.00 V to 0.00 V, both processes carried out under stirred conditions.

Results and discussion

Elemental Analyses

The carbon, hydrogen, and nitrogen analyses of the additives are shown in Table 1. The difference between 100% and the sum of percent C, H, N was taken as percent oxygen, sulfur and metal ion (which may occur with the lignin materials). The measured %N could be due to protein contamination. The empirical formulae obtained when nitrogen content is disregarded are given in the last column of the table. Only the ratio of the number of carbon atoms to hydrogen atoms can be derived since the oxygen content is not known. The C:H ratios obtained agree with those reported by Brauns (14), who obtained a ratio of 9-10 carbon atoms to 10-14 hydrogen atoms.

Table 1. Carbon, hydrogen, and nitrogen analyses of additives*					
Additive	%C	%H	%N	% O, S, metal	Empirical Formula, % N ignored
BL	39.68 ± .96	3.57 ± .47	.89 ± .23	55.86 ± 1.65	C ₁₀ H ₁₁ O _a S _b
CL	40.26 ± 1.61	4.40 ± 0	.08 ± 0	55.26 ± 1.60	C ₁₀ H ₁₃ O _c S _d
IN	60.67 ± .099	5.20 ± .11	.76 ± 0	33.37 ± .21	C ₁₀ H _{10.2} O _e S _f
SO	46.52 ± .20	3.40 ± .035	0	50.08 ± .24	C ₁₁ H ₁₀ O _g S _h
SH	33.68 ± .15	2.86 ± .14	.40 ± .014	63.06 ± .30	C ₁₀ H _{10.2} O _i S _j
* Average of two trials					

Uv-Visible Spectroscopic Studies

Absorption characteristics. The wavelengths (λ_{\max}) at maximum absorption for the five commercial and the dye in 1 M H₂SO₄ are summarized in Table 2. The occurrence of common peaks at around 220 and 280 nm suggests that the additives have similar components and/or structural features for calcium ligninsulfonate, indulin, sodium oxygignin, and sodium huminate. Differences in the λ_{\max} values may be attributed to many factors, e.g. differences in preparation, degree of sulfonation in water, pH, etc.

Table 2. UV - visible absorption of additives in 1.0 M H ₂ SO ₄	
Additives	λ_{\max} , nm (± 1)
Bulgarian lignin	232, 255
calcium ligninsulfonate	226, 282
indulin	224, 282
sodium oxygignin	218, 284
sodium huminate	214, 284
sodium alizarinsulfonate	262, 422

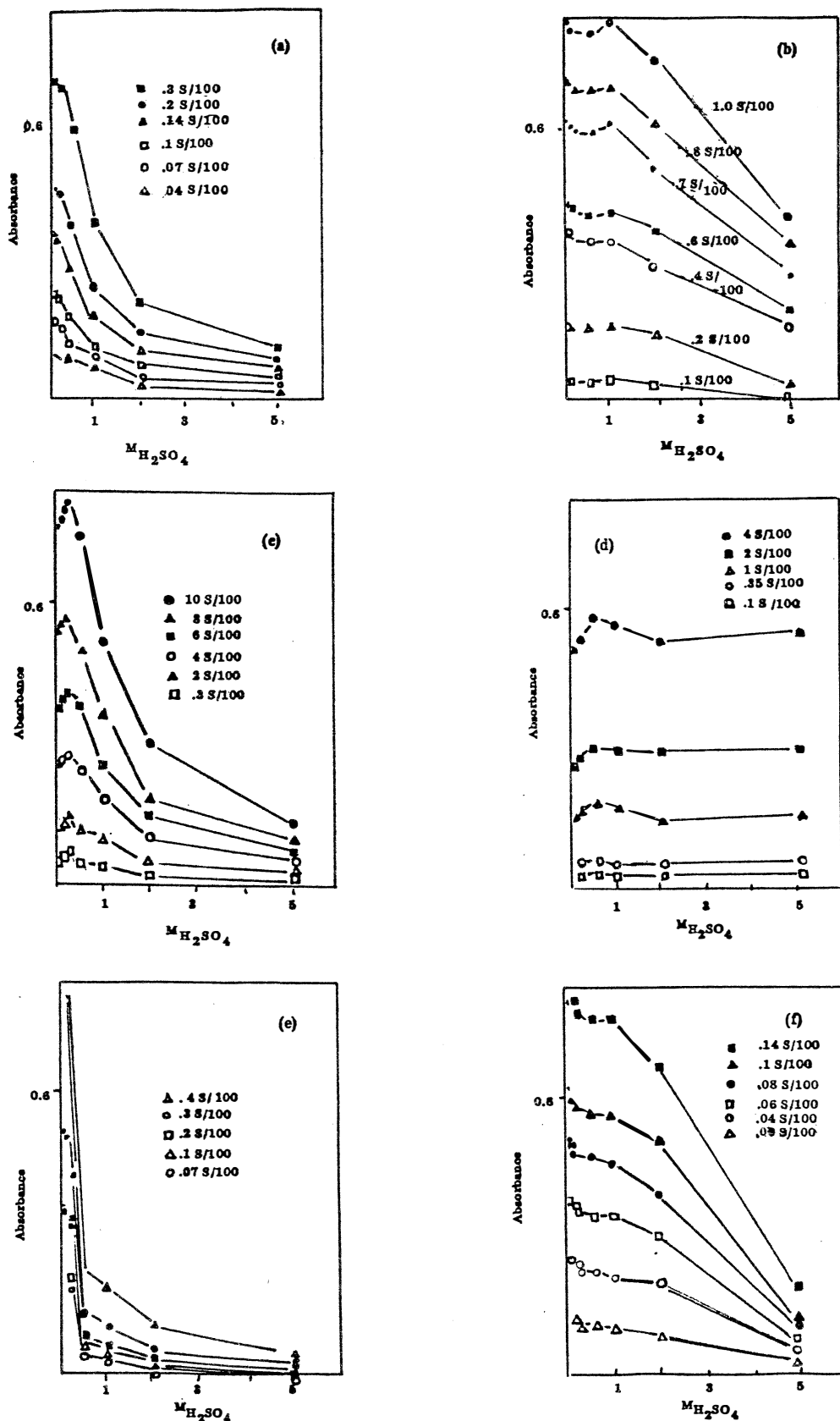


Figure 1. Absorption of various concentrations of additives in different concentrations of sulfuric acid. (a) BL at 232 nm; (b) CL at 282 nm; (c) IN at 224 nm; (d) SH at 214 nm; (e) SO at 214 nm; (f) SA at 262 nm.

The maximum absorption of the different dilutions of the filtered saturated additive solutions are typified in Figure 1 (a-f). The general behavior at all additive concentrations were similar, i.e., the measured absorbance decreased both with decreasing additive concentration and with increasing sulfuric acid concentration.

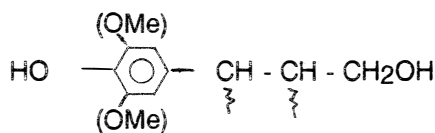
Bulgarian lignin and sodium oxylignin both showed exponential decrease in absorbance with increasing acid concentration. Calcium ligninsulfonate and indulin showed maximum absorbance values at 1.0 M H_2SO_4 and 0.1 M H_2SO_4 , respectively, but gradually decreasing at higher acid concentration. Sodium huminate yielded relatively constant absorption over the entire acid concentration range. Sodium alizarin gave high absorbances over a wider range of acid concentration, decreasing dramatically only at 5 M H_2SO_4 . The additives exhibited qualitatively similar behavior of absorbance versus acid concentration at the longer absorption wavelength (cf. Table 2) and may be found in Pablo's work (13).

The absorbance data show that the additives are generally more soluble in dilute acid solutions. Since high concentrations of acid are employed in lead-acid batteries (about 10% w/v H_2SO_4), apparently very small amounts of the additive must be actually involved in the "expander" action on the lead electrode.

Stability studies. The change in maximum absorbance was measured after the additive solutions (both filtered and unfiltered) had stood for 65 days. The average difference in absorption is 0.03 absorbance units for Bulgarian lignin, calcium ligninsulfonate, sodium oxylignin, and sodium huminate; in contrast, indulin and sodium alizarinsulfonate gave an average difference of 0.10. The absorbance readings fluctuated randomly, with the greatest difference between the two types of solution generally occurring in the early stage. No appreciable shifting of λ_{max} was observed.

Infrared Spectroscopic Studies

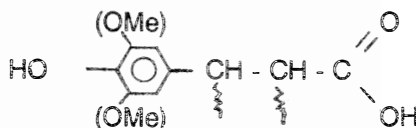
Characteristic spectra of the solid additives. Table 3 summarizes the absorption bands in the IR spectra of the original solid additive. From the structural features, (a) may be a possible structure common to the additives.



(a)

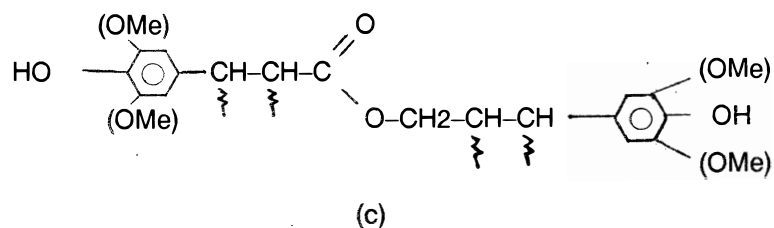
Stability studies. Residues were recovered for IR analysis from saturated solutions of the additives in 1.0 molar sulfuric acid after being stored for various lengths of time. It is noted that several additives, including calcium ligninsulfonate, Bulgarian lignin, sodium oxylignin, sodium huminate, and indulin, became colloiddally dispersed in the medium after standing in the acid solution for different periods of time and could not be analyzed.

Recovered residues of Bulgarian lignin (from one-day old solution), indulin (from one-, 10- and 30-day old solution), and sodium oxylignin (from one- and 10-day old solution) gave essentially similar IR spectra as the original solid. However, sodium huminate (from one-, 10- and 30-day old solution) exhibited distinct changes in spectra, as indicated in Table 4. Absorption bands at 2820 cm^{-1} and 1590 cm^{-1} disappeared at 2600 cm^{-1} (possibly due to $\text{C}=\text{O}$ stretching), 1290 cm^{-1} , 1180 cm^{-1} (possibly due to CO stretching), and 1010 cm^{-1} . Some changes suggested are oxidation of the aliphatic hydroxyl groups to carbonyl, forming (b),



(b)

and perhaps subsequent ester formation of the carbonyl group with unaltered hydroxyl group, forming (c),



or with the aromatic hydroxyl group, forming (d),

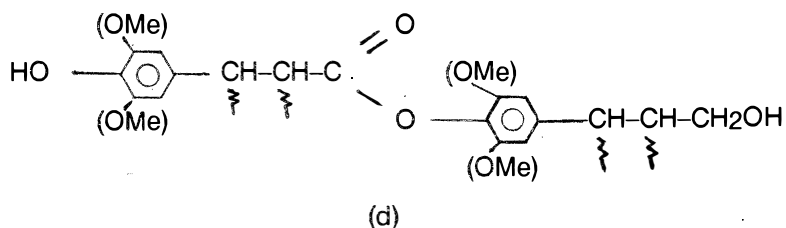


Table 3. Assignment of infrared absorption bands of the additives

Position in cm^{-1}					Band Origin
BL	CL	IN	SO	SH	
3400	3400	3400	3400	3400	OH stretching (H-bonded)
2920	2920	2920	2920	2920	
2880	2880			2880	
	2820			2820	
	1715				Carbonyl stretching – unconjugated ketone and carboxyl groups
		1650	1650		Carbonyl stretching – para substituted aryl ketone
1600–1590	1600–1595	1590	1590	1590	Aromatic skeletal vibrations
1510	1515–1510	1510	1510		
1450	1470–1460	1460	1460	1460	CH deformations (asymmetric)
1410–1400	1425	1425			Aromatic skeletal vibrations
1280	1270	1270	1270		Guaiacyl ring breathing with CO stretching
1210	1210–1200	1210	1210		
1145	1145	1145	1145		Aromatic CH in-plane deformation
	1130	1130			
	1085	1085	1085	1085	C-O deformation, secondary alcohol and aliphatic ether
1040	1035	1035	1035	1035	Aromatic CH in-plane deformation, primary alcohol

Table 4. Infrared absorption bands in (cm^{-1}) of sodium huminate after standing in 1.0 M sulfuric acid at various lengths of time.			
Number of days in acid			
Original solid	1 day	10 days	30 days
3400	3400	3400	3400
	3150		
2920	2920	2920	2920
2880	2880	2880	2880
2820	2820	2820	2820
	2600 (sh)*	2600	2600
	2300	2300	2300
	1715–1710	1715–1710	1715–1710
	1680	1680	1680
	1625	1625	1620
1590			
	1550 (sh)		
1460	1460	1460	1460 (sh)
	1400		
	1290	1290	1290
			1220
		1200	
	1180	1180	1180
1085	1090	1090, 1080	1080
1035	1035	1035	1035
		1010	1010
* (sh) shoulder			

Thin-Layer Chromatographic Studies

Different solvent systems were tried to effect the best separation of the components in the additives (13). However, generally only one spot (none in certain cases) was obtained, with relative retention factors (R_f) between 0.027 to 0.116. Little or no solute movement occurred when the solvent system contained a nonpolar component, such as ethyl ether or CCl_4 . The greater affinity of the additives towards polar solvents confirmed their polar nature. However, probably because of their relatively high molecular weights, migration from the origin of the TLC plate was limited.

High-Performance Liquid Chromatographic Studies

Of the two mobile phases tried (methanol and 4:1 (v/v) methanol-60% acetic acid), methanol generally resulted in better separation of the components of the additives, yielding four to six sharp peaks. Methanol-acetic acid not only gave fewer (three to four) peaks but also poorer resolution, and some peak tailing. Table 5 gives

the observed peak heights, p , and the corresponding retention times, t_R , in the two mobile phases. The retention times obtained were reasonably reproducible except in the case of Bulgarian lignin using methanol as mobile phase.

The poor separation obtained with methanol-acetic acid as mobile phase may be attributed to the protonation of oxygen atoms of the additives by acetic acid, producing species with comparable polarities and making their separation more difficult. Furthermore, the higher polarity of the methanol-acetic acid mixture (which actually contains some water) compared to methanol may have led to hydrogen bonding with the polar moieties in the additives, thus levelling the rate of migration of the components of the additives, and, consequently, giving poorer resolution.

Table 5. High-performance liquid chromatography of additives

	<u>Methanol</u>				<u>Methanol-Acetic Acid</u>			
	<u>Trial 1</u>		<u>Trial 2</u>		<u>Trial 3</u>		<u>Trial 4</u>	
	t_R , min.	p , cm	t_R , min.	p , cm	t_R , min.	p , cm	t_R , min.	p , cm
(a) BL	2.95	3.20	3.54	6.10	2.20	0.25	2.20	0.25
	3.94	2.50	4.43	2.10	4.63	8.50	4.63	10.40
	6.50	4.40	7.18	10.40	7.48	7.70	7.58	8.30
	6.79	4.00	8.07	1.10				
	7.48	1.60						
(b) CL	3.64	0.10	3.54	0.10	4.72	0.10	4.72	0.10
	4.53	0.70	4.23	0.50	5.71	0.15	5.51	0.15
	5.91	0.50	5.71	0.40	6.99	0.70	7.28	0.90
	6.69	0.90	6.30	0.60	7.48	3.60	7.68	0.90
	7.48	2.90	7.38	2.80				
	8.17	1.80	8.07	1.10				
(c) IN	3.74	1.60	3.74	1.50	4.63	2.60	4.43	2.40
	4.63	0.30	4.63	0.30	7.18	1.05	7.09	0.95
	7.28	3.00	7.28	3.00	7.68	1.30	7.68	1.15
	8.07	1.70	8.07	2.10				
(d) SO	3.64	1.05	3.64	0.50	4.53	1.40	4.53	1.50
	4.62	0.75	4.43	0.15	6.99	2.50	7.18	2.50
	7.18	14.70	7.18	1.47	7.58	7.20	7.77	7.20
	8.07	1.60	8.07	0.40				
(e) SH	3.15	1.60	3.15	0.60	4.43	4.60	4.43	5.00
	3.84	2.10	3.74	2.00	7.28	2.00	7.19	2.10
	4.53	0.55	4.53	0.85	7.68	4.20	7.58	4.00
	7.18	9.30	7.09	8.75				
	7.58	3.60	7.48	4.50				
	8.27	1.05	8.07	1.80				

Peaks occurring at approximately the same retention times suggest very similar structures for the additive component. The component present in greatest amount (i.e., the tallest peak height) in all additives had a retention time of 7.38 ± 0.20 minutes, using methanol as mobile phase; in contrast, the component with the tallest height using methanol-acetic acid as mobile phase was apparently not the same for all the additive, since the retention times were quite differing amount in each additive. In addition, it appears that there are other components, none of which seem to be common, present in calcium ligninsulfonate, Bulgarian lignin, and sodium huminate, but not found in sodium oxylignin nor indulin.

Linear Scan Voltammetric Studies

Figure 2 depicts typical anodic linear scan voltammograms on a smooth lead electrode in 1.0 M H_2SO_4 and in 0.1% (w/v) of a saturated solution of Bulgarian lignin in 1.0 M H_2SO_4 . Qualitatively very similar voltammograms were obtained in the presence of the other additives (13). Generally, starting from zero volt (vs. SCE), the lead oxidation process gave voltammograms with peak currents at around 0.92 ± 0.18 V. On further scanning in the positive direction, the current decreased, indicating inhibition of the dissolution process, and thereafter gradually increase again, signifying the onset of another anodic process, probably involving the formation of lead(IV) oxides and/or the oxidation of water to oxygen.

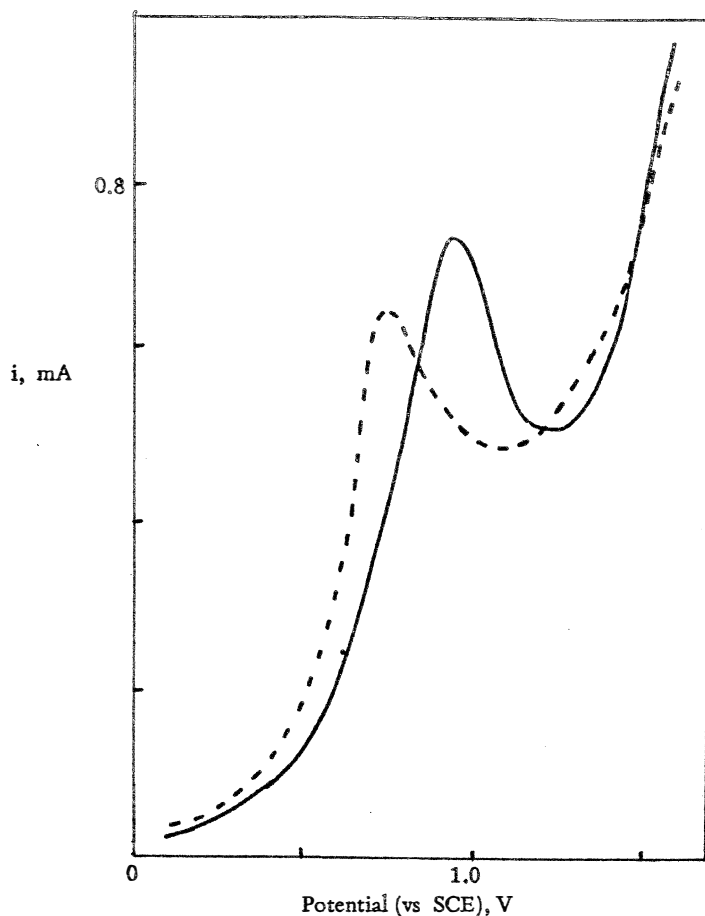


Figure 2. Linear scan voltammogram of lead at a potential scan rate $100 \text{ mV}\cdot\text{s}^{-1}$. Solid curve: in 0.5 M sulfuric acid alone; dashed curve: with 0.1% Bulgarian lignin.

The peak potentials measured in the presence of the additives generally occurred at less anodic values than in the absence of additives (see Table 6). The observed differences (ΔE_p) in anodic peak potentials became negligible for some additives (BL, SO, SA) after the additive solutions had stood for 35 days. This same trend was observed in 0.01% (w/v) additive solutions and in 0.5 M H_2SO_4 . These observations suggest that the anodic dissolution mechanism is not the same for the different conditions employed and is probably associated with

The peak current (i_p), measured at the peak potential, behaved in a much less consistent fashion than the peak potential. The ratio of the peak current obtained in the presence of additive to the peak current in sulfuric acid alone would be expected to be less than unity to be consistent with the inhibiting action of the additive. However, this ratio was the case only in fresh solutions of some additives (BL, IN, and SA), as seen in Table 6. CL, SO, and SH gave ratios larger than unity, as well as some aged solutions of BL, IN, and SA. These data reflect experimental variability of the electrode surface; the pretreatment procedure could expose different faces of the lead electrode, with varying roughness and, hence, varying surface areas. In view of this, E_p data are more reliable parameters for monitoring dissolution of lead.

Table 6. Anodic linear scan voltammetric data: lead in 1.0M H ₂ SO ₄			
Additive (0.1%)	Length of storage (days)	$\frac{(i_p)^+}{(i_p)^0}$ ^a	ΔE_p ^b (volts)
BL	1	0.94	-0.16
	7	1.20	-0.19
	14	1.50	-0.21
	23	0.64	-0.23
	35	0.97	-0.07
CL	1	1.50	0.00
	7	1.90	-0.18
	14	1.70	-0.15
	23	0.52	-0.29
	35	1.30	-0.14
IN	1	0.40	-0.15
	7	1.10	-0.21
	14	1.00	-0.07
	23	0.33	-0.29
	35	0.50	-0.14
SO	1	1.40	0.24
	7	2.00	-0.23
	14	1.40	-0.18
	23	0.57	-0.03
	35	0.76	0.00
SH	1	1.50	-0.01
	7	1.10	-0.05
	14	1.20	-0.05
	23	0.27	-0.29
	35	1.20	-0.14
SA	1	0.40	-0.15
	7	1.20	0.06
	14	1.30	0.11
	23	0.82	-0.16
	35	0.63	0.00
^a $\frac{(i_p)^+}{(i_p)^0}$ = $\frac{\text{Peak current in presence of additive (mA)}}{\text{Peak current in H}_2\text{SO}_4 \text{ alone (mA)}}$ ^b $\Delta E_p = (E_p) \text{ with additive} - (E_p) \text{ without additive}$			

Anodic linear scan voltammetry in 0.1% (w/v) additive solutions on a non-regenerated lead electrode surface yielded no anodic processes, signifying that the lead surface has been covered with solid PbSO_4 , thus inhibiting any further reaction of lead. This confirms that the negative plates of the lead-acid battery lose their discharge capacity when covered with a passivating film of PbSO_4 .

Chronopotentiometric Studies

Figure 3 shows chronopotentiograms of lead in 1.0 M H_2SO_4 and 0.1% (w/v) or saturated solutions of the different additives in 1.0 M H_2SO_4 at constant applied currents of 2.8 and 7.1 microamperes. A constant potential is seen to be attained within 40 seconds. Higher applied currents (1.0-25 milliamperes) resulted in the instantaneous change of potential, which could not be measured with the equipment available.

Two parameters were measured from the chronopotentiograms: the time (t) taken to reach the constant potential (E_c). The constant potential was attained within 10.6-29.8 seconds at the higher applied current, compared to 12.3-40.6 seconds at the lower applied current. Furthermore, E_c was reached more slowly (taking 14.6-40.6 sec) in the presence of the additives than in sulfuric acid alone (requiring only 10.6-24.3 sec). In both experiments, E_c generally occurred at less anodic values in the presence of additives, which is in agreement with the linear scan voltammetric findings.

Chronopotentiometry was performed at different times in additive solutions (in 1.0 M H_2SO_4), which was stored for a total of 69 days. E_c increased slowly with time of standing, and continued to increase at faster rates after approximately 30 days. In the presence of additives, E_c increased with time, changing +0.006-0.013 V/day. In the absence of additives, E_c was essentially constant at +0.868 V at an applied current of 2.8 μA ; however, the potential increased with time (changing 0.0010 V/day) at an applied current of 7.1 μA .

These data likewise imply the alteration in the structure of the additives, and a change in the mechanism of the dissolution of lead. The second possibility may also be true at very high applied currents even in the absence of any additives.

Voltammetric Titration of Additives with Lead(II)

On the hypothesis that lead(II) ions react with the additives through complexation, voltammetric titration of the 0.1% (w/v) or saturated solutions of the additives in 1.0 M nitric acid against lead(II) solution was performed. Anodic stripping voltammetry at mercury-filmed glassy carbon electrode was performed after each addition of Pb(II) ions to determine the amount of unreacted (uncomplexed) lead ions. Typical stripping voltammograms are shown in Figure 4 (A) for different volume increments of Pb^{2+} added to sodium oxylignin solution. The peak potential in all voltammograms occurred at -0.458 ± 0.010 V vs. SCE, corresponding to the oxidation of Pb(0) to Pb(II) in the supporting electrolyte used. The peak current, i_p , was measured as the perpendicular distance between the peak and a baseline drawn through the minima on either side of the peak.

Figure 4 (B) shows the voltammetric titration curve (i_p vs. $V_{\text{Pb}^{2+}}$). With the exception of Bulgarian lignin, all additive solutions did not yield any stripping peak upon addition of 0.10-0.30 mL of 100 ppm lead nitrate solution; beyond these additions, stripping peaks were observed and i_p increased with amount of added Pb(II) ions. From the amount of reacted Pb(II) ions, it appears that the dissolved additive concentration was between 5×10^{-7} - 1.4×10^{-6} moles/liter. In the case of Bulgarian lignin, a stripping peak ($i_p = 42 \mu\text{A}$) was already observed with the first addition of Pb(II) , and i_p increased with further additions of Pb(II) ions. This suggests that Bulgarian lignin may contain some lead or a similar metal ion, or has a much lower lead complexing capacity than the other additives.

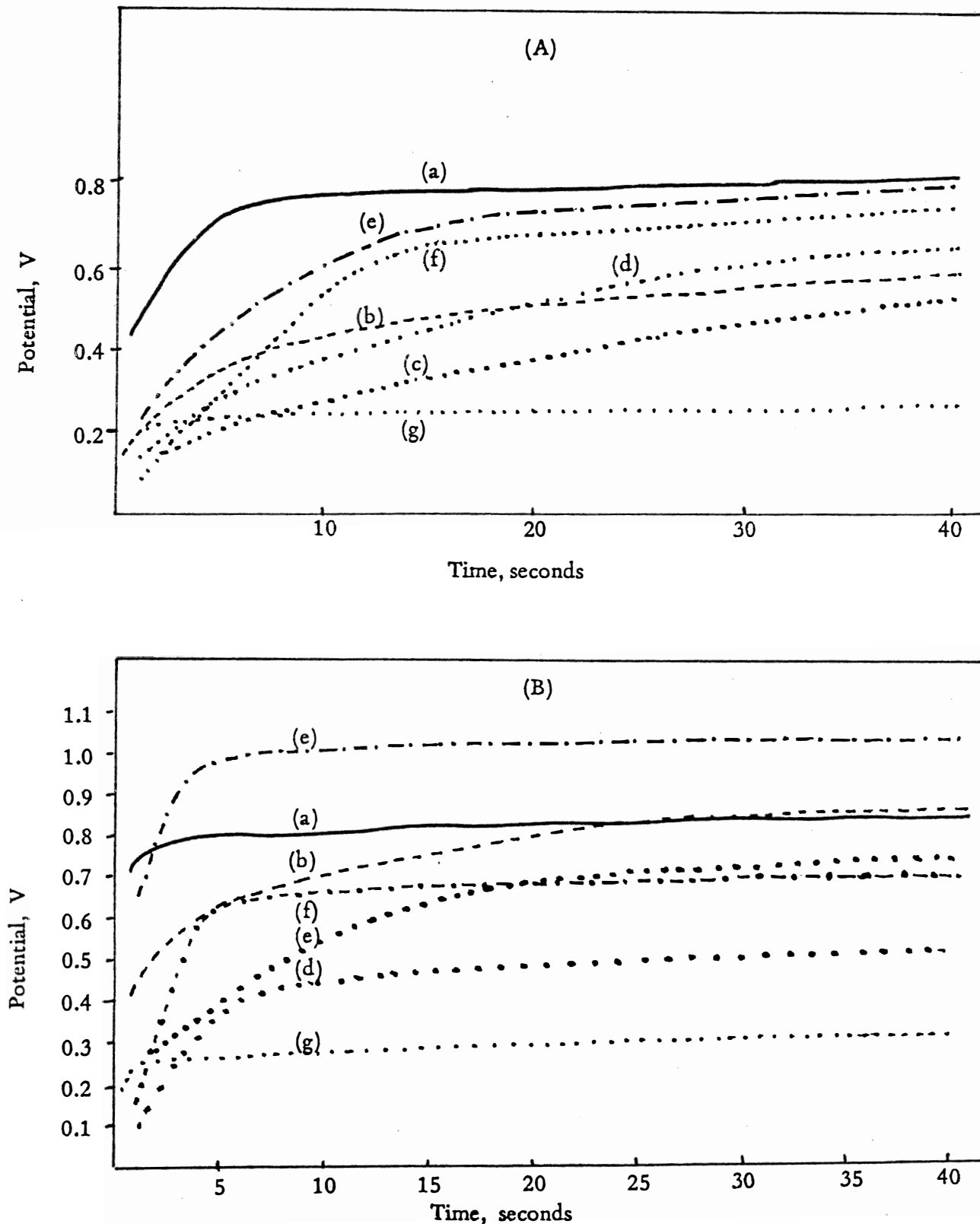


Figure 3. Potential change with time in 1.0 M H_2SO_4 at constant applied current of 2.8 μA (A) and 7.1 μA (B). (a) without additive; in 0.1% solution of: (b) BL, (c) CL, (d) IN, (e) SO, (f) SH, and (g) SA.

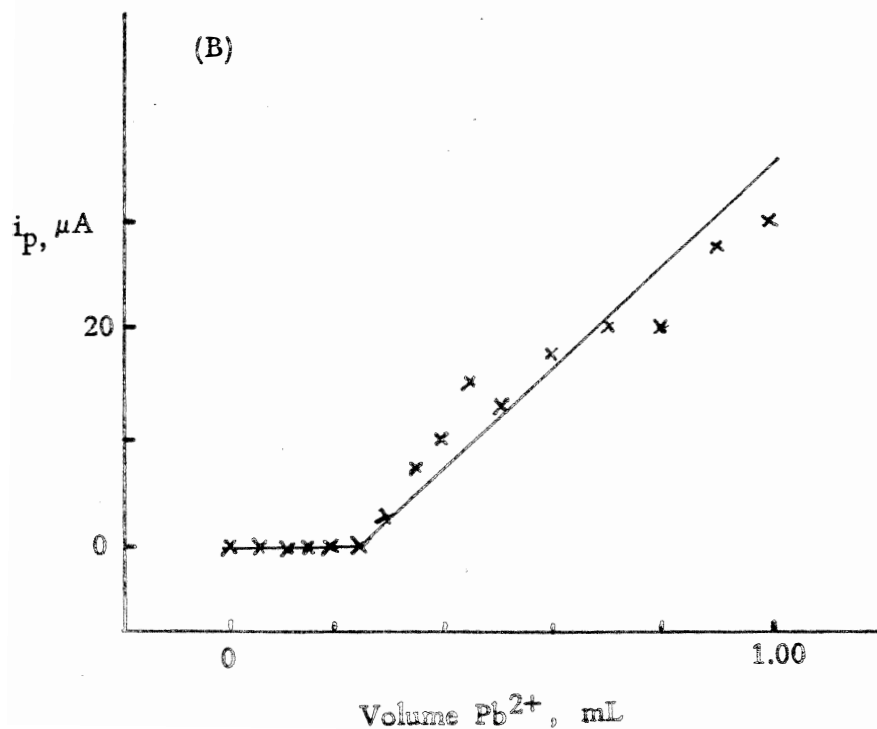
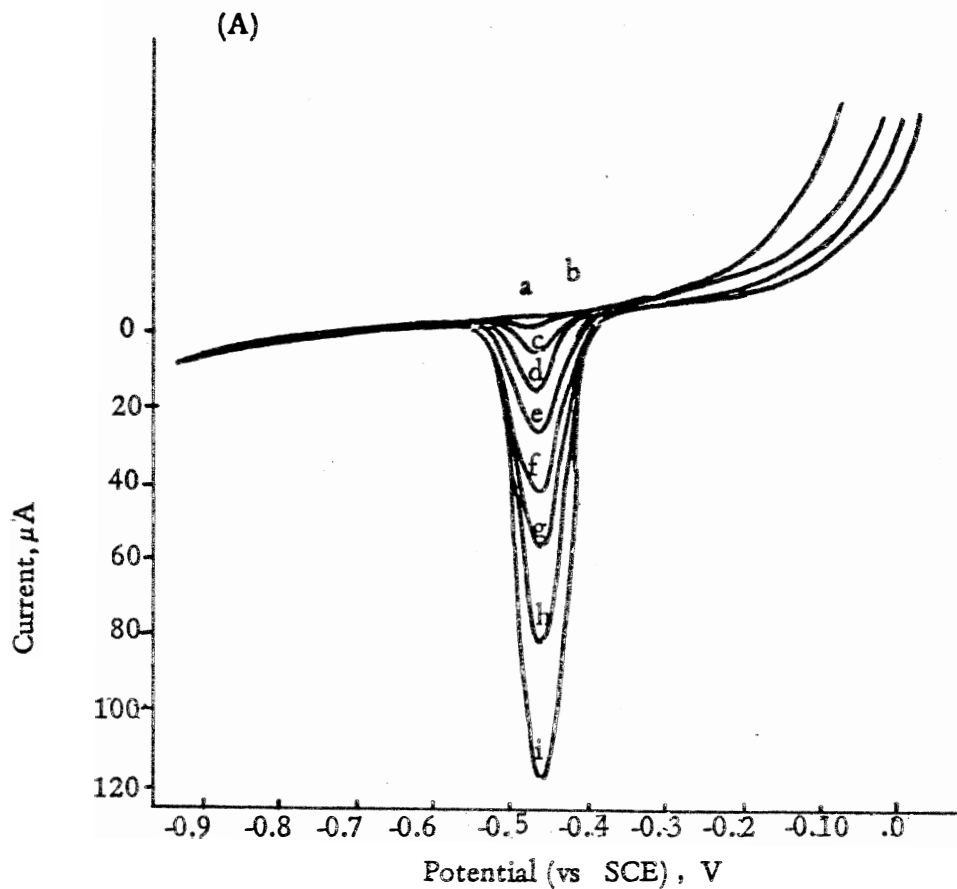


Figure 4. A. Anodic stripping voltammograms at mercury-filmed glassy carbon electrode of 0.1% solution in 1.0 M H_2SO_4 after addition of different volumes of lead(II) solution: (a) 0.00 to 0.25 (b) 0.30 (c) 0.40 (d) 0.80 (e) 1.00 mL. B. Voltammetric titration curve.

Conclusions

The elemental analysis and chromatographic results demonstrated that the additives are large, polar heterogeneous substance consisting of several different components but possessing similar structural moieties. The ultraviolet and infrared absorption spectra and elemental analyses indicate that the additives may include repeating units of aromatic residues substituted with etherified or free hydroxyl groups.

The commercial additives and sodium alizarin dye appear to have generally similar effects on the anodic dissolution behavior of the lead electrode.

Data from linear scan voltammetry and chronopotentiometry suggest that lead dissolves readily in the sulfuric acid solution by the solid-state mechanism of Archdale and Harrison (5,6). However, in the presence of the additives and during the early days of storage in acid, the dissolution-precipitation mechanism is apparently preferred, as evident from the more negative value of the anodic dissolution potential.

Prolonged storage of additives in sulfuric acid resulted in more anodic lead dissolution peak potentials, suggesting (in consonance with evidence from the IR spectroscopy) modification of the structure of the additives, thus rendering them ineffective, and leading to a return to the solid-state mechanism.

The voltammetric titration studies demonstrated that the lead ions formed during discharge (i.e., anodic dissolution of lead) may bind by absorption onto the large structure of the additives, or chemically by complexation, as suggested by Mahato (15). The transport of the Pb^{2+} to the electrode surface may also be hindered by the additive in this manner.

It may be inferred from this study that the beneficial action of the additive on the lead-acid battery comes from preventing the formation of a passivating film of lead sulfate crystal on the negative (lead) electrode surface during the oxidation process. Instead, the formation of more extensive but discrete nuclei or "micro-electrode ensembles" is apparently enhanced, ensuring a larger percentage of the theoretical capacity of the battery restored during recharge.

The production of lead-acid batteries would therefore benefit from the presence of organic additives like mill dusts during the electroformation of the negative plates. Similarly, the incorporation of about 0.01% (weight/volume of electrolyte) additive when recharging batteries may improve the discharge capacity.

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