To: Our Battery Friends around the World

From: Akiya Kozawa and John C. Nardi

(ITE Battery Research Institute)

Our lead-acid battery activator (organic polymer added to the acid electrolyte) produced the following excellent results over the past 18 years (1992-2010).

1. We have developed a new type of activator, an organic polymer (soluble in the acid electrolyte). U.S. Patent 5,958,623 (September 28, 1999) and U.S. Patent 7,160,645 (January 2, 2007). Five persons have obtained PhDs from Yamagata University from 2000 to 2008 based on this new activator technology.

2. The lead-acid battery is heavy. Therefore, its future use is considered to be limited for electricity storage using the solar cell system or similar areas. We can now reduce the engine starting battery weight. We know that the power density of a lead-acid battery is 160 W/Kg, which is 3 times that of lithium ion batteries. Therefore, we can reduce the lead battery size to 1/3 or less when used for hybrid cars. This means for hybrid car applications, the lead battery with out polymer activator may compete with lithium batteries.

3. Our basic research indicates that the main action of our polymer activator is to increase the hydrogen overvoltage of the negative electrode. Because of this, the hydrogen evolution from the negative electrode is reduced and a complete charge of the battery is achieved. Therefore, no sulfation takes place, or the existing sulfation is automatically reduced.

4. We tested 200 truck batteries with our activator addition once a year for 10 years. During the 10-year period, no battery replacement was needed in ary of the 200 trucks.

5. In another test, 50% smaller batteries were used. For example, an 80Ah battery was used in place of the 150Ah battery for 10 or 20 ton trucks. During the 4 year period, no battery deterioration was found. This indicated that we can reduce the battery size by 50% for SLI uses.

6. Because of the polymer activator, we can reduce the hydrogen evolution at the negative electrode; the short battery life (2 years in hot areas of the world) can be extended to 3 or 4 years.

7. Another possibility is the use of a slightly impure lead for lead batteries, since the impurity surface is covered by the organic polymer molecules and the hydrogen evolution is substantially reduced.

8. Deep discharge batteries with 30–50% deterioration were found to recover these capacity (Ah) with our activator addition after 2 to 3 month operation.

We hope our research will substantially contribute to abusing reduce the waste battery amount and help contribute to the environment since the life extension is certain to be 2 to 3 times greater.

ITE Battery Research Group (Japan and U.S.A.)
Dr. Akiya Kozawa, John C. Nardi, Shnzo Mase.
Advisors: Prof Y. Ohba, Prof S. Minami (Yamagata University and Osaka City University), Dr. R.J. Brodd (IBA: Board Chairman)

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How to Use ITE's Organic Polymer Activator for Recovery of Deteriorated Lead-Acid Batteries

By John C. Nardi, Tatsuya Shibano, Ralph J. Brodd and Akiya Kozawa
(ITE Yeager-Kozawa Battery Research Group (Japan))
Fax: 81-(0)52-459-4488,

Abstract:

In 1995, the ITE Battery Group discovered a new organic polymer activator for rejuvenating deteriorated lead-acid batteries; i.e., SLI (starting, lighting and ignition) batteries and deep cycle batteries. The research group has tested this new activator in various lead-acid batteries that are used in trucks, buses, taxis, golf carts, forklifts, etc. in Japan, India, China and other countries.

The deteriorated batteries having a discharge capacity of only 20-30% of their original capacity can be regenerated to 60-90% of their original capacity and that the recovered battery can be used for more than 3 to 5 years.

In this paper, the regeneration process using a special charging procedure is described and the process of the how this organic polymer works is explained.

1. Introduction

ITE's activator was developed in 1995 based on a composite of ultrafine carbon and an organic polymer (1). This composite material was soon thereafter patented (2). Later, we found that the organic polymer activator, called Super-K, can effectively recover deteriorated batteries, namely, remove the sulfation of the negative electrode (3). Ordinary truck batteries currently in use have a life of 3 to 4 years. The original capacity decreases with use, typically decreasing to 20-30% of the original capacity with continued use.

In this paper, a new and simple method for the recovery of these deteriorated batteries is described and the possible reaction mechanism of the organic polymer is presented.

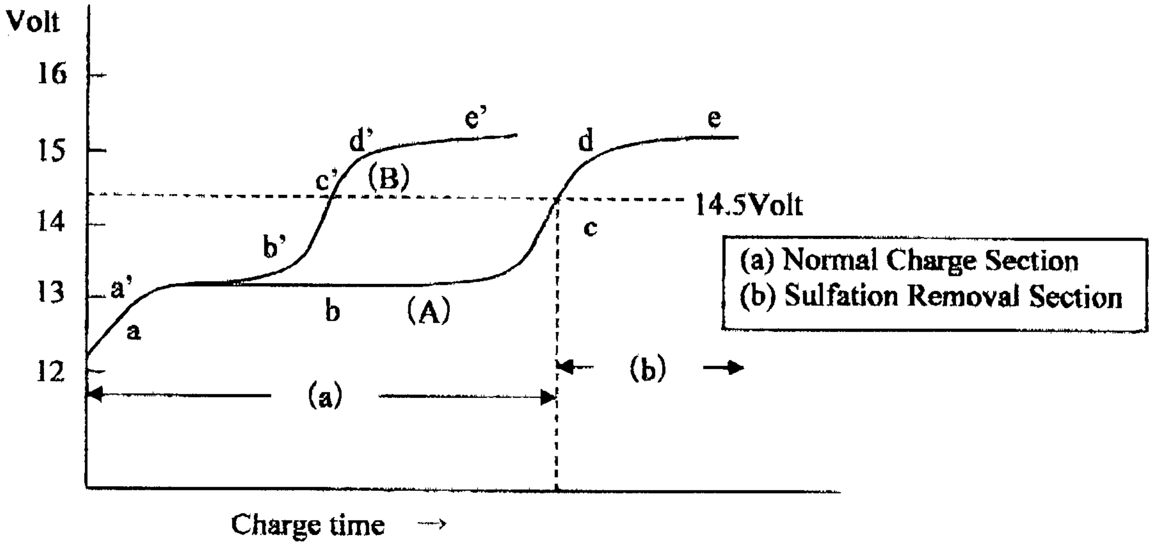
2. Experimental (Practical Operation)

We recommend the following processes (1 and 2). Process (1) is for batteries still in use, while process (2) is for deteriorated batteries that have been removed from a car, truck, etc.

(1) Add 0.5-1.0 grams of activator (tablet or powder) to each cell of 50 to 80 Ah batteries or 1.0-2.0 grams per cell for 100-150 Ah batteries.

(2) The deteriorated and replaced batteries require a special two-step charging after the activator addition.

The battery deterioration (capacity reduction to 20-30% of the original capacity) is recovered by removing the sulfation as follows. After the addition of water and activator (ITE tablets or powder), charge the battery one, two or three days as shown in Fig. 1 in order for the voltage to increase.



(A) a-b-c-d-e normal new battery
(B) a'-b'-c'-d'-e' 3-4 year's old deteriorated battery (having only 20-30% capacity of new battery)

Figure 1. Voltage increase during charging

Section (a) of Fig. 1 is for charging the good active material ($PbSO_4$) while section (b) is for charging the sulfated material at a low current that requires one or two days. When the battery is used for 3 to 4 years in a truck, car, etc., the negative electrode accumulates large deposits of crystalline $PbSO_4$ (by sulfation) and the dischargeable metallic lead becomes small due to a decrease in the active surface area. In the presence of our organic polymer in the acid solution, the polymer molecules are adsorbed onto the $PbSO_4$ and the metallic lead surface. Upon discharge, the chemical reaction, $Pb \rightarrow Pb^{2+} \rightarrow PbSO_4$ occurs. The $PbSO_4$ is produced in the presence of the organic polymer molecules, therefore, the crystal size of the $PbSO_4$ is small and porous (or amorphous), which has a high surface area and is still very active for the electrode reaction. For the charging process of the negative electrode, $PbSO_4 \rightarrow Pb^{2+} \rightarrow Pb$ (metal) occurs. In the presence of the organic polymer molecules, the metallic lead is likely to be very fine particles that have a very high surface area which is expected to be acitve for a good discharge reaction.

As shown in Fig. 1 (A) and (B), when the battery becomes old, the active material of the negative electrode becomes smaller, therefore, the charge curve goes from (A) for a new battery to (B) of the deteriorated battery that is most likely 3 to 4 years old. If the battery is in section (A), it can be charged at a high current (0.1C – 0.05C). However, if the battery is in section (B), it can only be charged at a low current (0.01C – 0.02C) since large crystalline $PbSO_4$ is very slow to dissolve. We recommend the following charge currents for (a) and (b). Also shown in Table 1 is the amount of activator (c) to add to each cell of the battery.

Table 1. Recommended charge current and activator for battery regeneration using ITE's organic polymer.

Section	Ampere-Hour Capacity of Pb-Acid Battery		
	40 – 60 Ahr	80 – 100 Ahr	130 – 200 Ahr
(a)	5 – 25 amps	5 – 8 amps	8 – 10 amps
(b)	0.4 – 0.5 amps	0.8 – 1.0 amps	1.2 – 2.0 amps
(c)	0.5 – 1.0 g/cell	1.0 – 2.0 g/cell	1.5 – 3.0 g/cell

The first activator charge operation requires one to two days, but the second and third charge-discharge cycles do not need more than one day each.

3. Results

Table 2 shows the results of the activator addition to 2-3 year old truck batteries during actual operation. We note that the specific gravity of the electrolyte increases over a 3-month period indicating that the sulfation is significantly reduced. Table 3 shows the same results for a battery used in a golf cart. After the activator addition, the specific gravity values were measured on Sept. 25th and Nov. 12th after a full battery charge. The specific gravity values of (B) are those before the activator addition. These results indicate that the activator addition increases the specific gravity thus showing that the batteries were improved, that is, regenerated.

Figure 2 shows the specific gravity increase for three forklift batteries four months after our activator addition during actual use of the battery. The results shown in Table 3 are those of regenerated used batteries (11 75-95 Ah truck batteries) in the two steps listed below after the addition of the ITE Activator (5% solution, 10 cc per cell).

First Step:	5-amp charge for 20 hours (corresponds to section(a) in Fig. 1)
Second Step:	2-amp charge for 68 hours (corresponds to section(b) in Fig. 1)

After each charge, the specific gravity of the electrolyte was measured. The results indicated that the specific gravity values increased as the sulfation was removed. The final battery test was done by a 75 amp discharge for 5 seconds. All the results indicated that these batteries are again suitable for use in trucks.

Table 2. Improvement of truck batteries using ITE activator

Battery 1 (155 AHr, one of two 12V batteries from a 10-ton truck containing a total of 240cc of additive)

	Cell1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6
Before addition Feb. 21, 2002	1.12	1.13	1.14	1.14	1.14	1.14
3 months later June 2, 2002	1.27	1.28	1.28	1.28	1.28	1.27
5 months later September 1, 2002	1.24	1.20	1.21	1.21	1.24	1.25

Battery 2 (145 AHr, one of two 12V batteries from a 10-ton truck containing a total of 180cc of additive)

	Cell1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6
Before addition June 2, 2002	1.21	1.21	1.20	1.18	1.18	1.20
1 month later July 21, 2002	1.26	1.25	1.25	1.26	1.26	1.25
3 months later September 1, 2002	1.25	1.25	1.27	1.27	1.25	1.25

Battery 3 (80 AHr, one of two 12V batteries from a 4-ton truck containing a total of 120cc of additive)

	Cell1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6
Before addition June 9, 2002	1.18	1.18	1.19	1.20	1.20	1.19
3 months later September 1, 2002	1.20	1.22	1.25	1.21	1.24	1.25

Battery 4 (145 AHr battery containing a total of 180cc of additive)

	Cell1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6

Before addition July 26, 2002	1.25	1.27	1.26	1.26	1.26	1.26
1 month later August 31, 2002	1.28	1.30	1.25	1.25	1.27	1.28

Table 3. Results of golf cart batteries

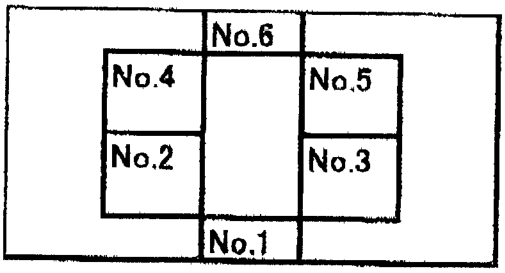
(All specific gravity measurements done after full charge, except on Aug. 20th.

比重表

Battery No.	No.1				No.2				No.3				No.4				No.5				No.6				
Cell No.	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	Voltage
(B)	1.28	1.28	1.28	1.28	1.28	1.27	1.28	1.28	1.25	1.24	1.11	1.24	1.28	1.27	1.27	1.28	1.28	1.28	1.28	1.28	1.28	1.28	1.28	1.28	49.2V
(A)	1.31	1.31	1.31	1.31	1.30	1.30	1.30	1.30	1.31	1.31	1.31	1.31	1.30	1.31	1.31	1.31	1.31	1.31	1.31	1.30	1.31	1.31	1.30	1.31	59.0V
8/20 1.5R	1.26	1.24	1.24	1.25	1.26	1.24	1.23	1.24	1.25	1.25	1.22	1.25	1.25	1.24	1.23	1.24	1.25	1.25	1.28	1.27	1.26	1.25	1.25	1.26	50.1V
9/25	1.31	1.29	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.27	1.30	1.30	1.30	1.29	1.20	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30	51.8V
11/12	1.30	1.25	1.30	1.31	1.30	1.30	1.30	1.30	1.30	1.30	1.27	1.31	1.30	1.30	1.20	1.30	1.31	1.20	1.30	1.31	1.30	1.30	1.29	1.28	50.8V

比重表

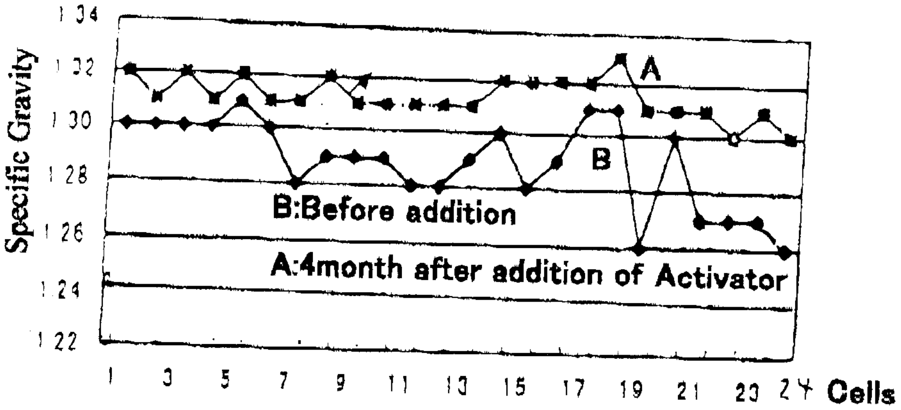
Battery No.	No.1				No.2				No.3				No.4				No.5				No.6				
Cell No.	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	Voltage
(B)	1.24	1.23	1.24	1.11	1.26	1.25	1.25	1.25	1.26	1.25	1.25	1.26	1.25	1.26	1.26	1.26	1.24	1.26	1.25	1.25	1.25	1.23	1.25	1.26	48.8V
(A)	1.31	1.30	1.30	1.27	1.30	1.29	1.29	1.28	1.30	1.28	1.28	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.29	1.29	1.30	51.2V
8/20 1.5R	1.27	1.29	1.29	1.27	1.27	1.28	1.26	1.27	1.27	1.28	1.27	1.27	1.27	1.27	1.28	1.27	1.30	1.30	1.30	1.26	1.26	1.26	1.26	1.26	50.8V
9/25	1.30	1.30	1.31	1.30	1.30	1.30	1.29	1.30	1.28	1.30	1.30	1.30	1.20	1.30	1.30	1.29	1.30	1.30	1.30	1.20	1.20	1.20	1.26	1.28	50.7V
11/12	1.31	1.31	1.31	1.30	1.30	1.30	1.30	1.31	1.26	1.29	1.30	1.30	1.26	1.30	1.27	1.26	1.27	1.31	1.30	1.18	1.20	1.27	1.28	1.27	50.6V



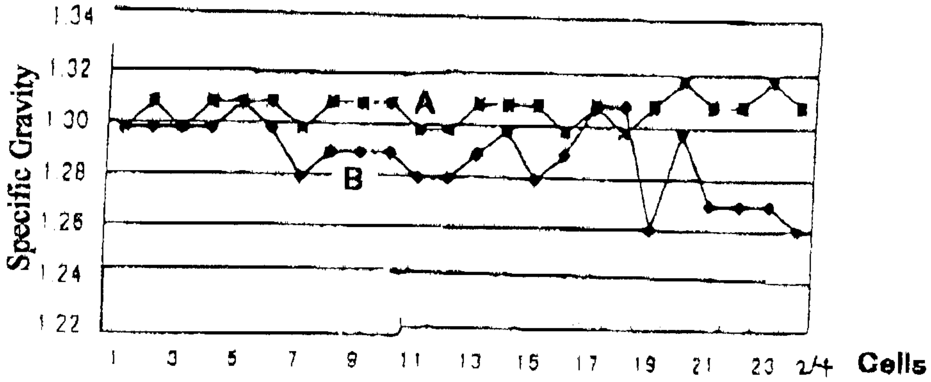
Battery arrangement in golf carts
(Battery: 8 volt, 150 Ah, Trojan brand)

(B) Before activator addition
(A) After activator addition
(8/20: after 1.5 round on Aug. 20th)

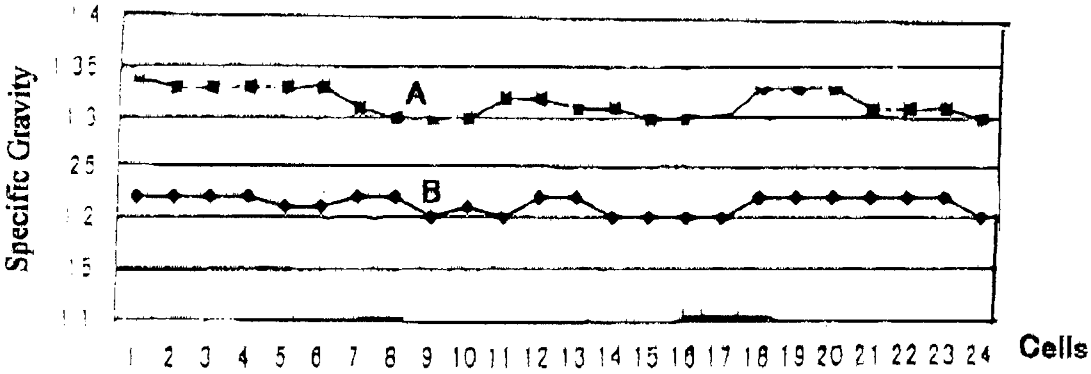
8/20, 1.5R (measured on Aug. 20th after 1.5 round, without charge)
9/25 (measured on Sept. 25th after full charge)



Forklift.1



Forklift.2



Forklift.2

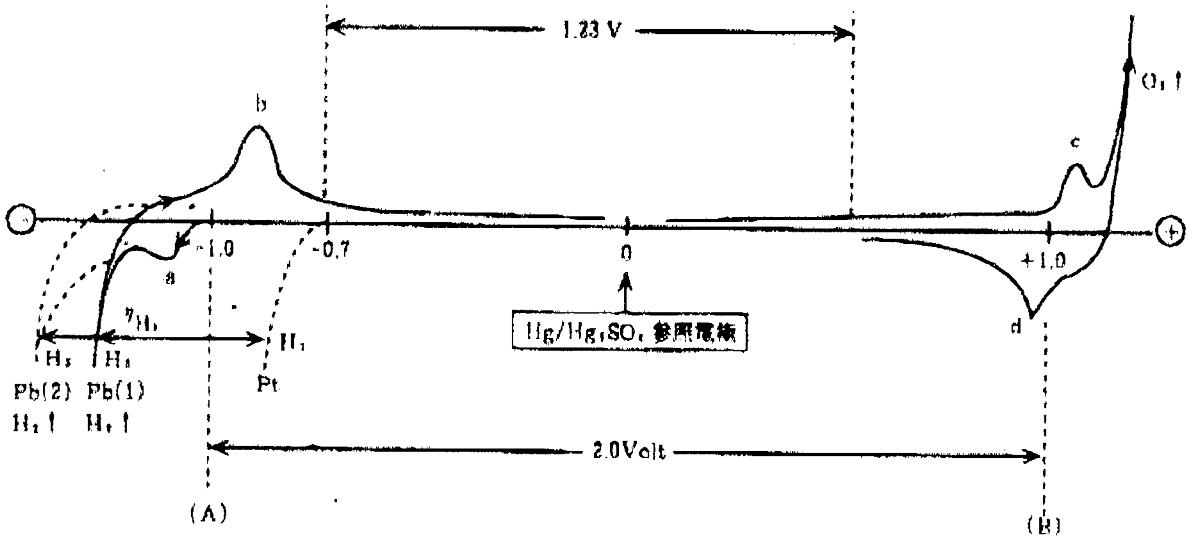
Figure 2. Specific gravity increase after activator addition

B: specific gravity before activator addition

A: specific gravity 4 months after activator addition

Table 4. Abandoned batteries regenerated by two-step charge.

Battery	New battery capacity (Ahr)	Measured capacity (Ahr) after 2A-18 hr charge	(1st step) specific gravity after 5A-20 hr charge	(2nd step) specific gravity after 2A-68 hr charge	Closed circuit voltage , 5 sec at 75 A
No. 1	75	6.8	1.27-1.28	1.30-1.31	11.55
No. 2	75	23.4	1.27-1.28	1.30	11.49
No. 3	75	51.0	1.26-1.27	1.31	11.73
No. 4	75	37.5	1.27-1.28	1.30-1.31	11.69
No. 5	75	75.7	1.30-1.31	1.32	11.98
No. 6	55	13.7	1.23-1.24	1.24-1.25	10.41
No. 7	55	22.8	1.23-1.24	1.24-1.25	10.72
No. 8	95	24.0	1.25-1.26	1.31-1.32	11.91
No. 9	95	29.6	1.25-1.27	1.30-1.32	11.94
No. 10	95	64.2	1.28-1.29	1.31-1.32	11.89
No. 11	95	4.3	1.27-1.30	1.27-1.31	11.69



(+) Electrode: $Pb \rightarrow Pb^{2+} + 2e$
$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

Side reaction: $H_2O \rightarrow H_2\uparrow$

(-) Electrode: $PbO_2 + 4H^+ + 2e \rightarrow Pb^{2+} + 2H_2O$
$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

Side reaction: $H_2O \rightarrow O_2\uparrow$

Total Reaction: $PbO_2 + 2H_2SO_4 + Pb \rightarrow PbSO_4 + 2H_2O + PbSO_4$

Figure 3. Reactions and Voltages of the Lead-Acid Battery

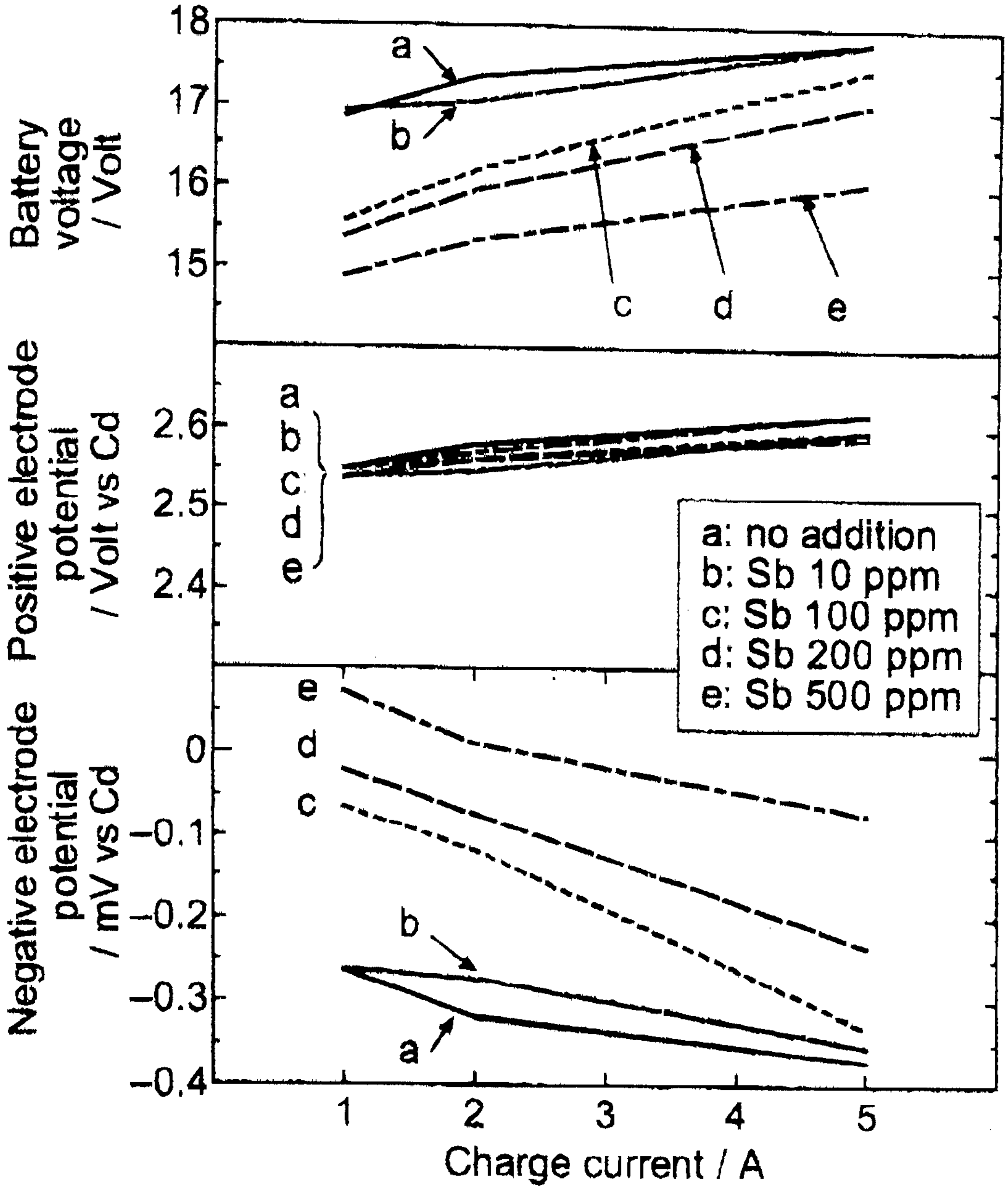


Figure 4. Effect of addition of various amounts of P-polymer solution to new 40 B-type car battery. The change in the electrode voltages were measured at 2, 5, and 10 ampere charge current.

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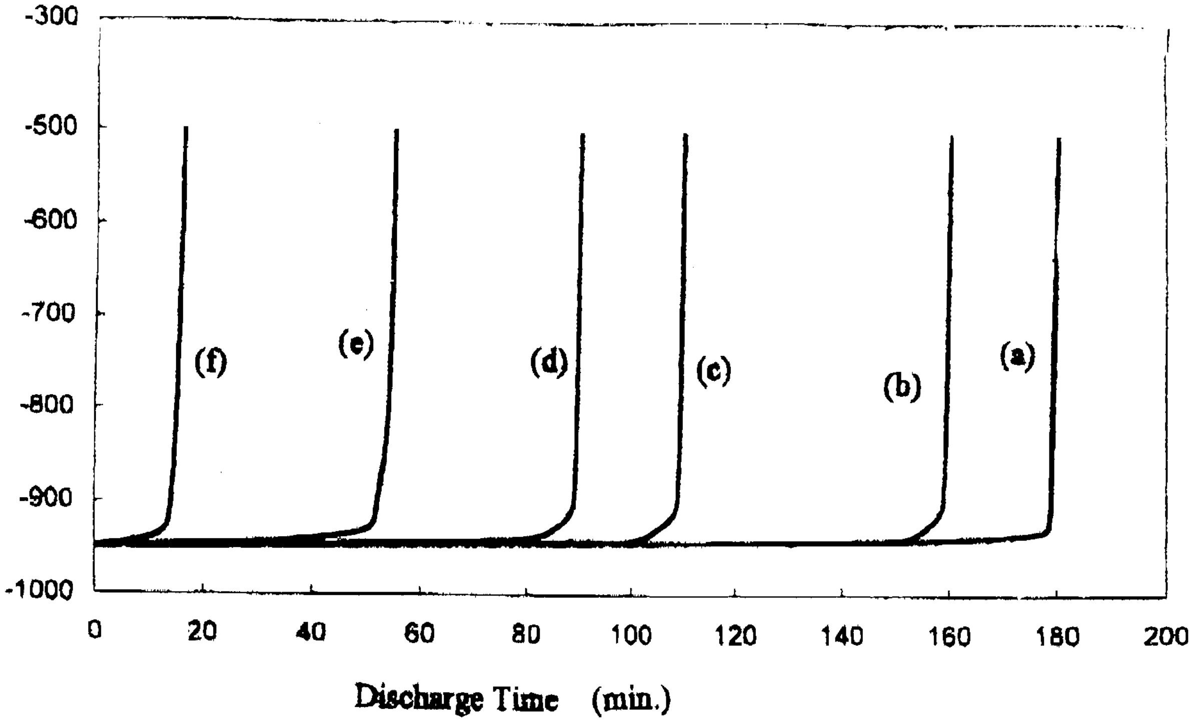

Figure 5. The effect of additives on the time to passivation of a pure lead electrode at a current of 0.1mA in 0.5M H_2SO_4. (a) no additive, (b) lignin, (c) $SnSO_4$, (d) polyvinyl alcohol, (e) acryl polymer(A), and (f) acryl polymer (B).

Table 1 Discharge Time to Passivation

	Additive	Discharge Time To Passivation (min.)
a.	No additive	180
b.	Lignin	160
c.	$SnSO_4$	110
d.	Polyvinyl alcohol	90
e.	Acrylic polymer (A)	55
f.	Acrylic polymer (B)	16

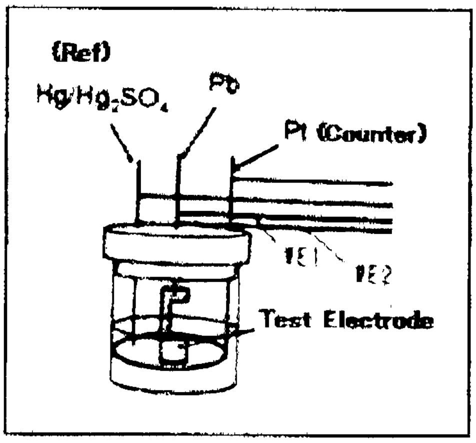

Table 4. Discharge Time to Passivation

	Additive	Discharge Time to Passivation (min).
A	No additive	180
B	Lignin	160
C	$SnSO_4$	110
D	Polyvinyl Alcohol	90
E	Acrylic Polymer (A)	55
F	Acrylic Polymer (B)	16

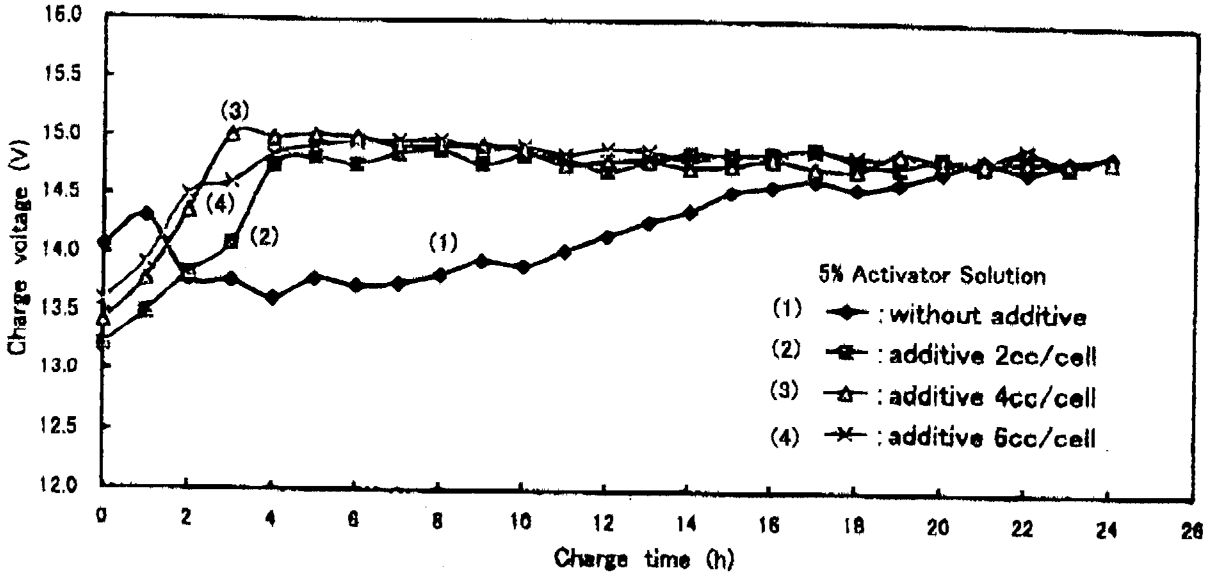

Figure 6. Battery voltage with or without activator. Deteriorated 38 Ah (38B20) batteries were charged by an SL-3 charger.

4. Discussion

Figure 3 shows the reactions and their voltages of the lead-acid batteries. The one-cell voltage is 2.1 volts (equilibrium voltage), but the actual open circuit voltage is about 0.5 volts greater than the hydrogen/water equilibrium voltage and oxygen/water equilibrium voltage. This means that the stable high lead-acid voltage of 2.1 volts (or 12.5 volts for a 6-cell battery) is based on the high hydrogen and oxygen evolution overvoltages. When we examine the hydrogen evolution on the lead electrode by cyclic voltammetry, the hydrogen evolution overvoltage significantly increased in the presence of the organic polymer in the acid solution, as indicated by the dashed line in Figure 3.

This higher hydrogen overvoltage in the presence of the organic polymer at the negative lead electrode was also confirmed in a commercial lead-acid battery (Fig. 4). Another experiment involving the lead electrode passivation at a constant current discharge is shown in Fig. 5. The voltage of the discharge curve quickly changes in the presence of the organic polymers (polyvinyl alcohol and acrylic polymers), since the hydrogen overvoltage is high due to the polymer molecule adsorption on the electrode.

Another experiment (Fig. 6) was done using deteriorated (abandoned) lead-acid batteries. Four abandoned batteries were obtained. ITE's organic polymer solution (5% PVA in water) was added at 2, 4 or 6 cc per cell in three batteries. One battery was tested without the polymer addition as the control. These batteries were charged using the SL-3 charger at 1.5 amperes overnight then discharged at 10 amperes to 9.0 volts. This charge-discharge cycle was repeated 24 times. The charge end voltages are shown in Fig. 6. Without the polymer activator, the battery voltage is low (13.5-14.0 volts) during the first ten cycles. All the other batteries having the polymer addition in the acid electrolyte had increased charge end voltages from 14.5 to 15.0 volts for the early cycles, i.e., after the third cycle. This indicates that the organic polymer is adsorbed on the negative electrode, thus the voltage increases and minimizes the hydrogen evolution. Without the organic polymer, the negative electrode produces a side reaction (hydrogen evolution), therefore, reduction of the sulfation is slow.

Based on these experiments, we can interpret the main beneficial action of the organic polymer as increasing the hydrogen overvoltage and effectively removes the sulfation from the negative electrode.

5. Long-term Practical Truck Tests

Based on the previously described research studies over a period of 15 years since 1990, we tested our ITE organic polymer activator in 200 working truck batteries used by the Sanwa Transportation Corp. located in Tokyo, Japan.

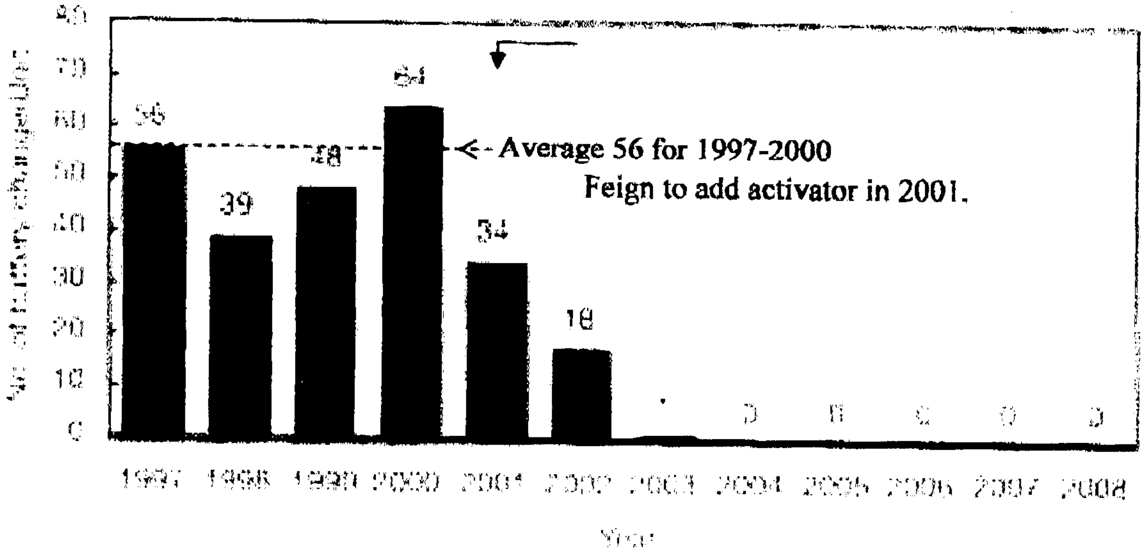

Fig. 7. Battery changes per year for 200 truck batteries used by the Sanwa Transportation Co. located in Tokyo, Japan (tel: 03-3866-6154, President: Mr. Konemasa Sakai)

The company has maintained good battery replacement records over the past several years. As shown in Fig. 7, the average battery replacement was 56 in 200 trucks used in our tests. In 1998, the replacement was very low (only 39) since the company purchased a large number of new trucks. We began to add our activator to the trucks in 2001 and the addition to all 200 trucks was completed in 2002. After 2003, the organic polymer activator addition was done once a year at the government inspection time. In Japan, such an official inspection for trucks, buses and taxis is required once a year by government regulation. At the inspection service shop, the added amounts of our activator are listed in Table 5.

Table 5. Amount of Added Activator

	50-80 Ahr battery	**100-150 Ah battery**	**160-200 Ah battery**
Avg. Amount	0.5 g/cell	1.0 g/cell	1.5 g/cell
Range	(0.5-1.0 g/cell)	(1.0-2.0 g/cell)	1.5-3.0 g/cell
	Excess activator addition had no negative effect on performance		

Since the completion year in 2003, no battery change was needed in their trucks. Therefore, it is suggested that the battery life is 8-10 years by adding our ITE activator once a year.

For private passenger cars, such a required government inspection is required once every two years. Thus activator addition would be done once every two years. However, the organic polymer activator is slowly decomposed by oxidation at the positive electrode, but this oxidation is very slow, since the large polymer molecules are slow to diffuse to the positive electrode.

6. Summary and Conclusions

1. Deteriorated batteries in use can be rejuvenated from sulfation based on the specific gravity increase during use in trucks, golf carts and forklifts when ITE's organic polymer activator is used. (Tables 1 and 2 and Fig. 2).
2. Deteriorated and abandoned truck batteries can be regenerated by a two-step charging operation after the addition of ITE's organic polymer activator.
3. The main beneficial action of the organic polymer is increasing the hydrogen overvoltage at the negative electrode.
4. The battery recovery from sulfation only slowly takes place by the charge-discharge procedure (Fig. 6).
5. The beneficial action of the polymer lasts 1-2 years. The lead-acid battery life can be extended to 8-10 years instead of 3-4 years with the yearly addition of the organic polymer activator.
6. Extending the life of used lead-acid batteries can significantly reduce the number of waste batteries, save energy and contribute to our green society.