

Research on Activators for Lead-Acid Batteries

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Abstract

The ITE Battery Research group has developed a new organic battery activator for new and used lead-acid batteries. Ten years of investigation have established the validity of the ITE activator that prolongs the useful life of lead-acid batteries. It has been shown that the specific gravity of spent batteries can be restored to the original level in automotive, motive power; uninterruptible power supplies (UPS) and stationary energy storage batteries. Our results show that the discarded batteries over 60% can be used for normal car service. Also, the activators were effective for the life extension even in the repeat of continuous high rate discharge, and maintained the original level up to 200 cycles in the ordinary conditions. This paper summarizes the basic concepts for life extension of lead-acid batteries by ITE activator and experimental results to justify the proposed concepts.

1. Introduction

Lead-acid batteries account for the largest segment of battery market. These batteries find applications in cars, trucks, and busses for starting, lighting, and ignition, motive power for fork lift trucks and golf carts, for energy storage in UPS and utility applications. The total worldwide market is approximately \$20 billion and is expected to grow significantly in the future as the economies of China, India and other countries approach that of North America, Europe, and Japan. The lead-acid battery has a price advantage over several other battery systems with competitive performance.¹⁾

Table 1 compares the cost and energy storage capabilities of several common rechargeable battery systems. The average automobile has a life of about 10 years. The average life of automobile battery life is 3 to 4 years. Batteries for hybrid gasoline-electric cars constitute an emerging market. In this market, cost and performance will determine the winner. The battery cost is a significant component in the cost of the vehicle. Currently,

Table 1 Relative and energy storage capability of common rechargeable batteries

Battery system	Style	Cost US\$/Wh	Capacity Wh/kg	Capacity Wh/L
Lead-acid	Automotive SLI	0.05	35	70
	Motive & Stationary	0.25-0.35	10-25	50-80
Ni-Cd	Sealed	0.25-0.50	20-35	40-100
Ni-MH	Sealed	0.30	110	300
Li-ion	Sealed	0.30-0.40	210	500

the life of the Ni-MH battery used in all hybrids is 3 to 4 years. With ITE activator, it should be possible to extend the lead-acid battery life to 6 to 10 years for this application provided it meets the cycle life and electrical performance requirements. Longer life lead-acid battery may fit this application and has the advantage that the recycling infrastructure is already in place.

2. Importance of improved performance with ITE activator

The ITE activator is a mixture of polyvinyl alcohol and inorganic salt, and has proved effect for

- (1) Recovery of deteriorated batteries from sulfation (They regain essentially their

original capacity and performance level)

- (2) Formation of high surface area electrode material for use in production of new batteries
- (3) Sulfation accounts for about 80 % of battery failure during use

The activator is not effective for problems related to loss of electrical contact, cracked electrical connection grid corrosion and the like.

The natural and synthetic lignins as organic additives are mixed to negative paste to improve the fluidity and plasticity. Their solubility is not high in the ordinary sulfuric acid electrolyte, and the significant effect of the lignin on the charge-discharge performance has not been obtained²⁾. Barium sulfate and carbon as inorganic additives added to negative plate have been also tried to prevent progressive growth of $PbSO_4$ and for better conductive paths^{2, 3)}. The ITE activators are soluble in the sulfuric acid electrolyte, and different from other additives. This is a unique try for the improvement of charge-discharge performance and life of the lead-acid battery. The activators developed by ITE are the polyvinyl alcohol containing sodium sulfate and other metal sulfates, and are supplied as P000, PNH2, and PN30 of the original brand name^{4, 5)}.

Proper use of the ITE activator results in extending the useful life of the battery up to 2 or 3 times. The life extension minimizes the environmental impact of the scrap lead-acid batteries. Most countries require the collection of scrap lead-acid batteries for recycling. According to statistics from Battery Association of Japan, over 90 % of scrap batteries are collected and recycled in Japan and the United States. In the 80 % of the areas of the world, the batteries have not been recycled, but land-filled for disposal. Our new technology will reduce the battery recycling process and make a great contribution to our environment. Such battery is named "Environmentally Friendly Battery"



Fig. 1 Environmental Friendly Battery produced by our technology in China.

by us as shown in Fig. 1¹⁾.

3. Mechanisms of battery deterioration

3.1 Regeneration of deteriorated batteries and standard test⁶⁾

Every car repair shops judge the battery deterioration by specific gravity of acid electrolyte. When the charge is insufficient, the specific gravity is below the specified value, and hence the values are not an indicator for battery deterioration. We proposed a simple standard test for the judgment of car battery deterioration. These tests include the following: (1) 150A-5sec discharge test (for engine starting), (2) an 80A continuous discharge test (for capacity measurement), (3) current-voltage (I-E) measurements, (4) specific gravity measurements (SG) for the acid electrolyte, (5) closed circuit voltage (CCV) and open circuit voltage (OCV) measurements.

Typical results for 150A test and I-E curve measurement are described in Table 2, Fig. 2

and Fig.3. The deteriorated (discarded) 40B car batteries (YO1 - YO6) were collected from car repair shop. One new battery (YN1, 40B type of Panasonic) was used for comparison. The batteries were first charged by SL-3 charger (Daijikoogyo Ltd.) for 24 h. This charger is an inexpensive commercial product that weights only 1.6 kg. The maximum charge current is 2.0-2.5 A. The voltage is not controlled, so the charging voltage can increase to 17.0-17.5 V. Most of the chargers for lead-acid batteries have a controlled voltage range of 13.8 to 14.4 V. Therefore, we cannot use those types of chargers for the reactivation process of converting the crystalline PbSO₄ to metallic lead (active material of negative electrode). This SL-3 charger can pass 0.5±0.1 A even when the battery voltage is 17.0 V or higher.

The result of 150 A discharge test for 40B battery (YO1-YO6 and YN1) is shown in Table 2. The test was done using the circuit shown in Fig. 2. To check a lead-acid battery for its engine starting capability, the 150A-5s

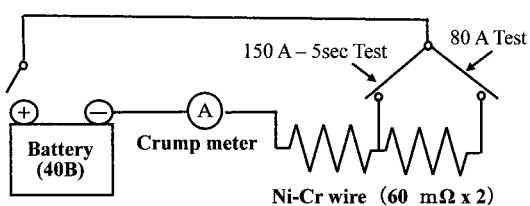


Fig. 2 150 A - 5 s discharge and 80 A continuous discharge tests of deteriorated batteries.

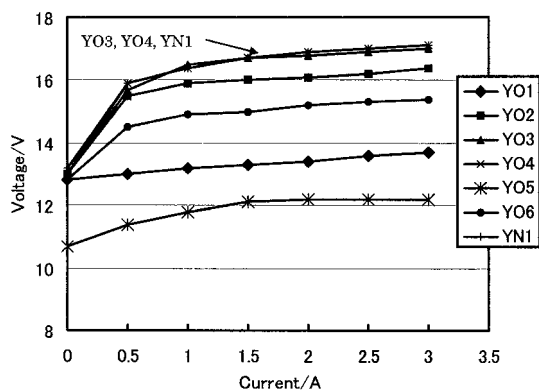


Fig. 3 Charge current - voltage curves of new and deteriorated lead-acid batteries.

discharge test is usually used. The CCV values after 5 s are read during the test. As long as the CCV is maintained at 10 V or higher, the battery is useful for engine starting purposes. Based on this result, 60% or above of the discarded batteries can be regenerated to a reuse state when a low current continuous charge is applied over 1day.

The charging current -voltage (I-E) curve measurements were done by taking CCV readings at 0.5, 1.0, 2.0 and 3.0 A. These results are shown in Fig.3. The I-E curve remains high for the new battery while the curve for the poor batteries, such as YO1 and YO5, is below 14 V. If the metal ions dissolved from the positive grid are deposited on the negative electrode, hydrogen evolution takes place and the I-E curve remains low (below 14 V). Therefore, the CCV at 1.0 A is a good measure to evaluate the battery. We can use the CCV at 1 A for the quick evaluation of the battery. Other tests such as 80 A continuous discharge, CCV and OCV measurements resulted in the same conclusions for the regeneration of deteriorated batteries. Among the six used batteries, four can be reused. This means that 66.6% of the discarded batteries can be used for normal car service.

The standard battery activation and regeneration methods are created for reducing waste batteries by prolongation battery life. If this method is fully utilized, we will significantly reduce the waste due to such batteries.

Table 2 Results in 150 A - 5 s discharge test.

Battery	Current / A	Voltage after 5 s / V	Evaluation
YO1	133.7	9.98	×
YO2	145.7	10.53	○
YO3	142.7	10.22	○
YO4	139.7	10.04	○
YO5	107.8	7.68	×
YO6	143.3	10.43	○
YN1	145.7	10.74	○

Evaluation

○: above 10 V or greater than 138 A, ×: below 10 V or less than 138 A

3.2 Observation of Sulfation

Our research group has proposed that the mechanisms for lead-acid battery deterioration are responsible for sulfation as the main reason⁷⁾. The sulfation means that the PbSO_4 particles on Pb negative electrode became larger in the size. The undischarged PbSO_4 slowly accumulates during the discharge at small current and self discharge. Accordingly, the subsequent charge and discharge are inhibited by passive layer of PbSO_4 with larger particle sizes, which is called the sulfation.

Figure 4 shows two steps involved in the discharge of negative electrode in the solution containing organic polymers. In the first step of the discharge, Pb^{2+} ions are produced on the electrode surface, and diffuse passing through the adsorbed layer of organic polymer to the bulk solution. Then the Pb^{2+} ions combine with H_2SO_4 to produce PbSO_4 . Because of the organic polymer layer, the Pb^{2+} ions can not diffuse out rapidly in the bulk solution and the Pb^{2+} concentration become much higher than the solubility of PbSO_4 in the 5 M H_2SO_4 , electrolyte, which is the normal lead-acid battery electrolyte. When precipitate of PbSO_4 takes place in the concentrated solution, the particles of PbSO_4 are fine and they have high surface area. Such PbSO_4 is easy to dissolve on discharge and provides an active (high rate) electrode. If the PbSO_4 particles are large and the surface area is low, it is slow to dissolve

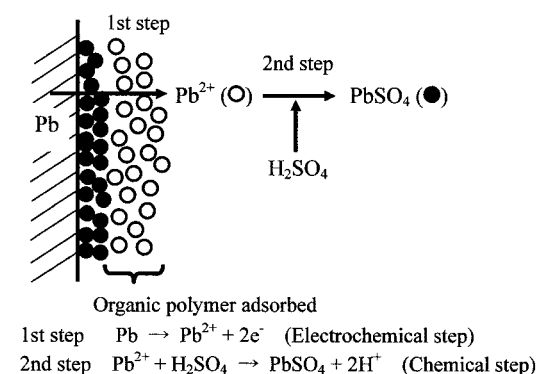


Fig. 4 Discharge process of negative electrode.

and the electrode discharge capability is poor. This is the sulfation on the negative electrode.

The effects of organic polymers on electrode surface have been experimentally confirmed by SEM observation after the cycles of charge-discharge⁸⁻¹⁰⁾. Figs. 5 and 6 show the SEM pictures of negative (Pb) and positive (PbO_2) electrodes after 20 cycles of the charge-discharge, respectively. Polyvinyl alcohol (PVA) was used as the organic polymer, and the other additives (POOO, PNH2 and PN30) were also tried in this experiment. The morphology shows the electrode surface covered with the PbSO_4 . Obviously, the negative electrode surface is uniformly covered with small particle sizes of PbSO_4 compared to that in 5 M H_2SO_4 of normal lead-acid battery electrolyte. There is no effect of organic polymers of the positive electrode surface. Accordingly, the sulfation takes place in the Pb negative electrode, and the organic polymers inhibits the sulfation. The protonated organic polymers in acid solution are predominantly adsorbed on the negative electrode to produce the PbSO_4 of fine particles in the adsorbed layer of the polymers as shown in Fig. 4. The chemical formation of PbSO_4 on Pb and PbO_2 powder has been also tried by redox reaction with H_2O_2 . The same results as that in the electrochemical reaction were obtained on the particle sizes on the Pb and PbO_2 corresponding to negative and positive electrodes¹¹⁾.

Hirai et al.^{3,12)} have reported that the fundamental studies of PbSO_4 crystal formation on the Pb electrode containing BaSO_4 , SrSO_4 and lignin as the additives of negative electrode paste by electrochemical atomic microscopy. The morphological studies are interesting in crystal growth, but the charge and discharge profiles have not been described. Recently, sodium salt of polyaspartic acid was reported as soluble organic additive to inhibit the sulfation¹³⁾. The results on the morphology of

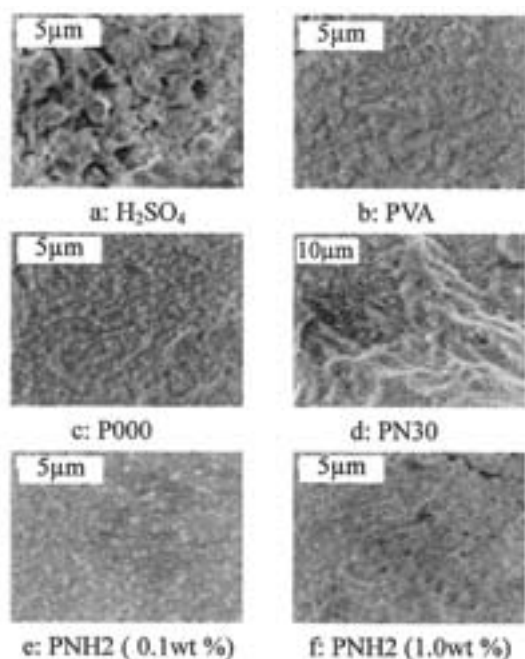


Fig. 5 SEM pictures of negative electrode surface after 20 cycles of charge-discharge.

PbSO₄ are comparable to the ones reported by the authors. This additive is low in solubility and high in price, and then limited for practical application.

Some metal ions are dissolved in the acid electrolyte from the grid material of positive electrode, and affect the reaction on negative electrode. The authors have reported that Ag⁺ ions activate the PbSO₄ formation on Pb negative electrode and that In³⁺ ions are effective for the negative shift of hydrogen evolution potential^{14,15}. The behaviors of these metal ions are supposed to be one of candidates as additives with organic polymers.

The typical cyclic voltammogram (CV) of Pb in the sulfuric acid electrolyte is shown in Fig. 7. The redox couple at -0.4 V corresponds to the oxidation of Pb to PbSO₄ and the reduction of PbSO₄ to Pb. The CV was recorded in the 5 M H₂SO₄ containing some metal ions (2x10⁻⁴ mol L⁻¹), and the anodic and cathodic peak currents were plotted for the standard electrode potential (E°) of metal/metal ion as shown in Fig. 8. The metal ions (Ag⁺ and Cu²⁺) with

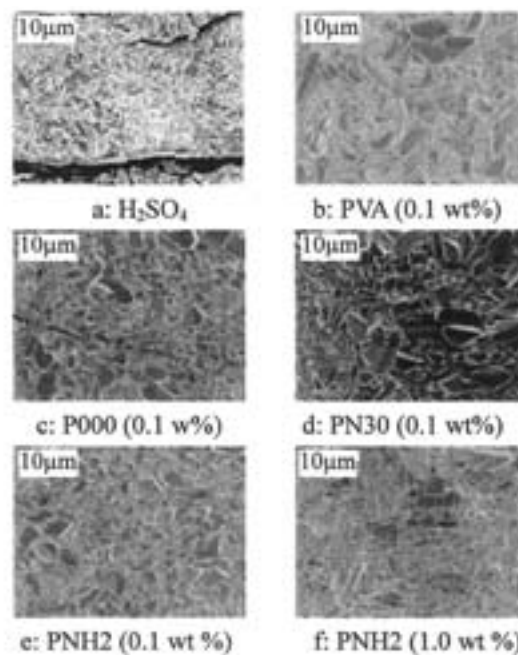


Fig. 6 SEM pictures of positive electrode surface after 20 cycles of charge-discharge.

higher electrode potential increased the current in the redox reaction of Pb and PbSO₄. There is no significant effect of the metal ions (In³⁺, Ni²⁺, and Sn²⁺) with lower electrode potential on the redox current of Pb and PbSO₄.

The SEM pictures of Pb electrode surface morphology were obtained after 20 cycles as shown in Fig. 9¹⁷. The Ag⁺ and Cu²⁺ give fine PbSO₄ particles, and there is no effect of other metal ions on the surface morphology compared to that in H₂SO₄ electrolyte. The Ag⁺ and Cu²⁺ ions deposit on the electrode to form adsorbed layer of metallic species on Pb electrode in the potential region of Pb and PbSO₄ formation, and the metallic species act as the adsorbed center of H₂SO₄ resulting in the formation of fine PbSO₄ particles. The further study is required for this speculation.

4. Battery performance and activators¹⁶⁻¹⁸⁾

It has been reported that the lead-acid batteries deteriorate by the sulfation on Pb negative electrode. The organic polymers are effective for the inhibition of sulfation, and

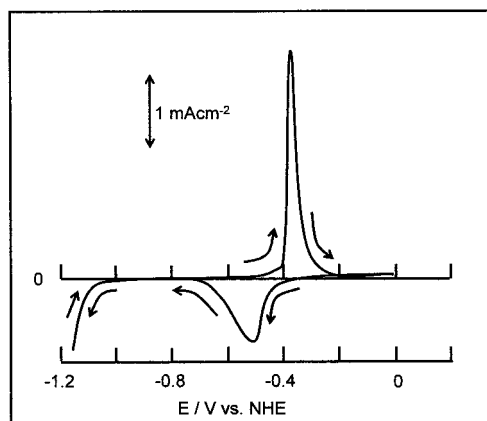


Fig. 7 Cyclic voltammogram of Pb at 20 mVmin⁻² in 5 M H₂SO₄.

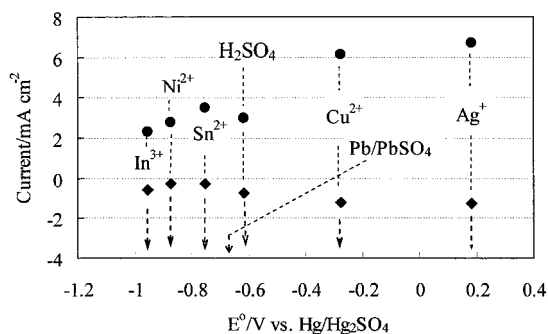


Fig. 8 Relationship between standard electrode potential (E°) M^{n+}/M (M : metal ion) and peak currents in cyclic voltammogram of Pb electrode in metal ion containing 5 M H₂SO₄ (metal ion concentration: 2×10^{-4} mol L⁻¹).

expected to improve battery performance and life. These additives are called the activator by the ITE battery research institute. The new batteries deteriorate by the sulfation during the cycles of the charge-discharge process. When the activators are added to the acid electrolyte of the new batteries in commercial, it is expected to prolong the battery life. The studies on performance of lead-acid batteries have been mainly carried out to improve the high rate discharge for cars and electric vehicles. To overcome this problem, grid design¹⁹⁾ and trace element control²⁰⁾ have been proposed. More recently, the use of expanded graphite as additive that improves the conductivity during operation was demonstrated²¹⁾.

The research group has investigated the effects of the activators on the performance and

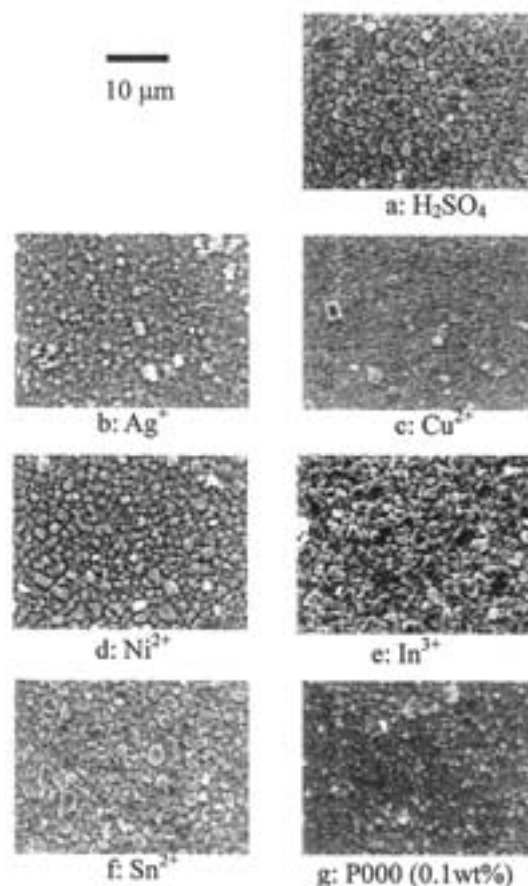


Fig. 9 Effect of metal ions on surface morphology of Pb electrode after 20 cycles.

battery life for the batteries in commercial. Figs. 10 and 11 show the typical results for the new car battery (40B) in Japan and the new battery for the semi-shield E-bike (12 V, 10 Ah) in China. The concentration of activator is shown in the figure captions. The car battery was discharged at high rate (90 A) and deep discharge (9 V), and the E-bike was discharged under the normal conditions. Both the car and E-bike batteries demonstrate that the activators are responsible for the life prolongation. For 40B car battery without activator, about 70% of the initial capacity (11-12 Ah) was maintained after 16 or 17 cycles. The activator (0.5g/cell) may enable to maintain the charge-discharge over 30 cycles. When the charge-discharge under ordinary conditions was repeated for the E-bike battery with activator, about 90% of the

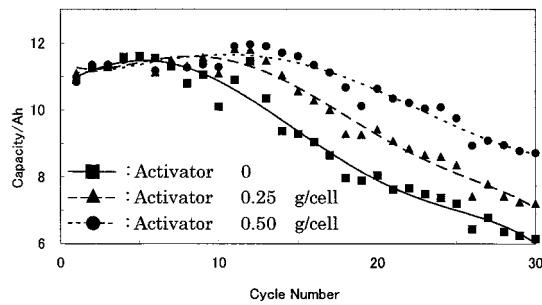


Fig. 10 Change in capacity discharged at 90 A to 9 V with cycles for the car battery (40B) with and without activator (PNH2). Charge condition: charged by SL-3 charger for 20 h.
 ■: activator: None, ◆: PNH2: 0.25 g/cell, ▲: PNH2: 0.5 g/cell

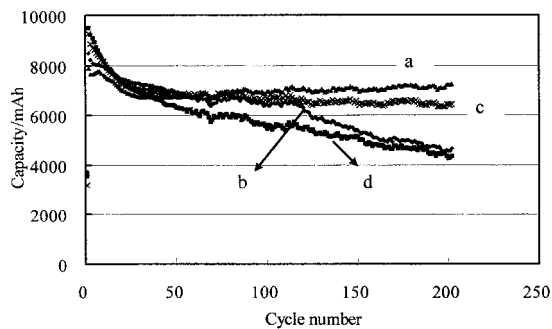


Fig. 11 Change in capacity with charge-discharge up to 200 cycles for 10 Ah semi-sealed 12 V batteries with and without activator (P000).
 □: Activator: None, ■: Activator: 1.5 g L⁻¹, ▲: Activator: 3.0 g L⁻¹.

initial capacity was maintained up to 200 cycles. These results show that the addition of activators is effective for the new battery in production process and commercial.

As shown in Fig. 10, the battery deterioration is improved even in the high rate and deep discharges. This indicates that the battery with activators may be used for hybrid cars. The use of activator also indicates the possibility of the battery with less amount of lead than that in the present battery assembly, because the activators prevent the battery deterioration. Such a new approach is being in progress for the new battery production as Low Lead SLI (starting, lighting and ignition) Battery¹⁾. The activator technology for lead-acid batteries can reduce waste battery, and therefore greatly

contribute to our environment. This environmentally advantageous battery has much lower price than current commercial products.

5. 200-Truck experiment in Japan^{22, 23)}

We selected 200 long distance trucks for the test by Sanwa Transportation Co., in Tokyo. The 5-10 ton trucks were mostly used, and each truck had two batteries (150 Ah, 12 V). Our experimental test started in April 2000 using the trucks with batteries already in use. The Company's records show that the average life of the truck batteries was 3.5 years. Thus, the company replaced batteries for 57 trucks (200/3.5) per year from 1997 to 2000 as shown in Fig.12.

The activator treatment of all 200 truck batteries was completed in two years from 2001 to 2002. Since 2003, there have been no battery replacements. The activator was added once a year when the water addition was done. The trucks using these batteries were being sufficiently charged. We realized that a sufficient charge was a key to extending the life expectancy of truck batteries.

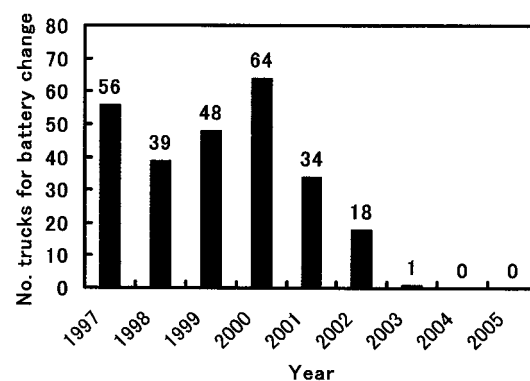


Fig. 12 Battery replacements per year among 200 trucks.

6. Conclusion

The ITE activator has demonstrated its capability to significantly increase the useful life lead-acid batteries in most applications. It also has noteworthy environmental impact by

lowering of the accumulation of lead in the environment. The anticipated expansion of the market for lead-acid batteries serves to emphasize the importance reducing environmental impact of lead. The ITE activators can give new life, a rebirth so to speak, for the 140 year old battery system.

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