CHLORINE IN THE LEAD STORAGE BATTERY

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The manufacturer of lead storage batteries has long been cognizant of the effect of chlorine on his product. Batteries sometimes bubble or "gas" while standing on open circuit, the positive plates become brittle and break up, the separators bleach and become soft and the battery itself loses charge. These phenomena are often correctly attributed to the presence of chlorine.

Chlorine is present in the storage cell only as an impurity and is not found in all or even many cells. It finds its way into the cells through impure battery water, through the use of impure materials of construction and, in rare cases, by the direct addition of salt water where the uninitiated tries to rejuvenate a cell in the same manner in which boys often successfully enliven a worn out dry cell. Its effect remains the same whatever the source of contamination. The purpose of this paper is to demonstrate these effects of chlorine and to point out how, when present, it may be removed.

EXPERIMENTAL

The original acid from a fully charged, five plate, storage cell was replaced with 425 ml. of 1.285 sp. gr. electrolyte to which had been added 8.186 g. of chlorine in the form of sodium chloride. Extremely vigorous gasing and a strong odor of chlorine was noticed immediately. The surface of the electrolyte was whipped into a froth by the escaping chlorine. Forty-five minutes after filling the battery the evolution of chlorine had become much less violent and a 5 ml. sample of the electrolyte was pipetted out for analysis. The method of analysis used in this experiment, as in all succeeding ones, was Volhard's. The electrolyte at this time contained 210.7 mgs. of chlorine per 100 ml. of solution, about one-ninth of the quantity originally present. Similar analyses 3 and 24 hours after the start showed the electrolyte to contain 106 and 22.4 mgs. per 100 ml. respectively. At the end of the 24 hour period the total voltage of the cell on open circuit was 1.84 volts, indicating that the battery was almost completely discharged. The cell was then put on charge and brought up to a condition of full charge at which time it contained no chlorine. Fifty-five ampere hours were required for this purpose, which is within 10 per cent of the capacity of the cell. The separators were bleached on the side next to the positive plates. They were very soft and under light rubbing by the finger tips easily disintegrated. The grids did not seem to be appreciably brittle in this case.

This experiment shows that chlorine in a battery will be eliminated even while the battery is standing on open circuit and that charging increases the speed with which this is accomplished. The bleaching of

"Proc. Ind. Acad. Sci., vol. 42, 1932 (1933)."

the separators on the side next the positive plates shows that the liberation of chlorine takes place at this electrode. The reaction resulting in the liberation of chlorine takes place between the combined chlorine and the active material of the positive plates. It is probably the same as that sometimes employed in preparing chlorine in the laboratory.

$$PbO_2 + 2HCl + H_2SO_4 \rightarrow PbSO_4 + 2H_2O + Cl_2$$

The fact that the positive grids did not become brittle in this experiment merely means that the chlorine was not present a sufficient time for this result to become apparent.

The loss of charge noted in this experiment was probably largely due to the reaction of the active material in the positive plates. That the negative plate can also be discharged by the presence of chlorine has long been surmised. According to this idea the chlorine liberated at the positive plate during charge dissolves antimony out of the positive grid. The dissolved antimony is then plated upon the active material of the negative plate and forms a short circuited couple with the negative active material. This short circuited couple discharges the active material of the negative plate. The following experiments were made in order to test this hypothesis.

Seven cells were set up in small glass beakers. The negative plates consisted of pieces cut from previously formed plates. The positive plates were made of solid antimonial lead. These were assembled in 1.200 sp. gr. acid and connected in series. To the first three cells salt was added in sufficient quantities to make 50, 100 and 1000 mgs. of chlorine per 100 ml. of electrolyte, respectively. The last four contained no chlorine. The cells were all given several cycles of charge and discharge at about 0.03 amperes per sq. in. of positive plate surface. A white precipitate appeared in the bottom of the first three cells, the most being in the one containing the most chlorine. In the others a deposit of brown lead peroxide was observed. The negative plates were removed from the acid, washed with distilled water and dried for analysis. A small amount of active material was scraped from each negative plate, care being taken not to remove any of the grid metal. These portions of active material were tested individually for antimony by the Marsh test. The four cells to which no chlorine had been added gave negative tests, while the other three all showed the presence of antimony. The amount of antimony was greater in accordance with the quantity of chlorine in the cells. The first cell, which contained only 50 mgs. of chlorine per 100 ml. of electrolyte, gave only a faint test, yet distinct enough to be plainly seen. Negative active material from the first three cells were also tested for arsenic and negative tests were obtained. This confirms the presence of antimony and proves that the chlorine causes it to dissolve from the positive grid after which the antimony is plated out on the negative active material. The removal of antimony from the positive grid leaves it easily attackable and the subsequent peroxidation of the grid produces mechanical weakness.

These experiments having shown how chlorine effects the storage cell, it was deemed advisable to determine the rate at which chlorine is eliminated from the cell. To this end the following experiments were performed.

To three cells of ordinary starting battery size, containing five plate elements, and whose electrolyte was adjusted to 1.285 sp. gr., 100, 200 and 400 mgs. of chlorine was added respectively, in the form of sodium chloride. The cells were given three cycles of charge and discharge. At the end of the second and third cycles 50 ml. portions of the electrolyte were removed from each cell for analysis. The results of these analyses are recorded in Table I.

TABLE I

Cell No.	Mgs. of combined chlorine per 100 ml. electrolyte		
	Start	End 2nd cycle	End 3rd cycle
1.	400	0.38	0.00
2.	200	0.22	0.00
3.	100	0.37	0.00

It is evident from this experiment that various amounts of chlorine are eliminated from batteries, by charging and discharging, in practically the same time so long as the quantities present are not great. By the end of the second cycle more than 99.9 per cent of the chlorine had been liberated, while all of it had disappeared by the end of the third cycle. From this it may be concluded that no battery in active service can long contain combined chlorine as chloride unless it has a constant source of contamination.

To these same cells, now fully charged and free from chlorine, sufficient salt was added to introduce 1000 mgs. of chlorine into each cell. This is approximately 200 mgs. per 100 ml. of electrolyte. The cells were then allowed to stand on open circuit and the electrolyte was analyzed at various times. The results are given in Table II.

TABLE II

Cell No.	6 days after start		10 days after start		14 days after start	
	mgs. present	% eliminated	mgs. present	% eliminated	mgs. present	% eliminated
1.....	3.2	98.4	0.56	99.7	0.46	99.77
2.....	1.4	99.37	0.48	99.75	none	100.0
3.....	1.26	99.4	0.77	99.6	none	100.0
Ave.....	1.95	99.0	0.60	99.7	0.15	99.92

This shows that the rate at which the last traces of chlorine are eliminated is extremely low. That is, the rate at which chlorine is evolved is proportional to the concentration of chlorine ions in the electrolyte. This was to have been expected from a consideration of the law of mass action. The reaction may also be expected to run to completion since the chlorine is liberated as a volatile product.

Other experiments were conducted showing that the rate of elimination is lower in stationary batteries where the gravity of the electrolyte is only about 1.210. Still other experiments were made demonstrating that when chlorine is added in the form of ammonium chloride it acts in the same way and is eliminated at about the same rate. In these latter experiments brittle positive grids were encountered.

General Discussion

Chlorine when present in the storage battery, enters into a reaction with the lead peroxide of the positive plates, the reaction resulting in the discharge of the plate and the release of free chlorine. The chlorine, being given off at the positive plate comes in contact with the separators on the side toward these plates. The free chlorine bleaches the separators, at the same time causing them to lose their hardness, toughness and tensile strength, thus diminishing their life.

Most of the free chlorine escapes from the battery, but a portion of it comes in contact with the antimony in the positive grid and dissolves it. During charge the chlorine ions liberated on the positive grid also dissolve antimony. This dissolved antimony is carried to the negative plate where it is plated out in a spongy form, thus forming a short circuited couple with the lead sponge, which discharges the plate. As the positive grid is depleted in antimony it becomes peroxidized and very brittle.

If the contaminated cell is allowed to stand on open circuit all of the chlorine is apparently eliminated. The rate at which this liberation takes place is dependent on the concentration of combined chlorine in the electrolyte. This rate may be greatly accelerated by charging and discharging.

Conclusions

The foregoing experiments show that:

1. Chlorine reacts with the lead peroxide in the positive plate causing its discharge and the release of free chlorine.
2. Chlorine dissolves antimony from the positive grid causing it to become easily peroxidized and lose its mechanical strength.
3. The dissolved antimony is plated out on the negative plate where it forms a short circuited couple and discharges the plate.
4. Chlorine bleaches the separators, at the same time causing them to lose their hardness, toughness and tensile strength, thus diminishing their life.
5. Chlorine is released from the surface of the positive plate as free chlorine.
6. The rate at which chlorine is released depends upon the concentration of combined chlorine in the electrolyte.
7. The rate at which chlorine is released may be greatly accelerated by charging and discharging.
8. Chlorine is eliminated from batteries with high gravity electrolyte at a greater rate than from batteries with low gravity electrolyte.