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POST OFFICE ENGINEERING DEPARTMENT

TECHNICAL PAMPHLETS FOR WORKMEN

Subject:

Maintenance of Secondary Cells.

ENGINEER-IN-CHIEF'S OFFICE 1919

LIST OF =

Technical Pamphlets for Workmen.

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MAINTENANCE OF SECONDARY CELLS

(G.1).

The following pamphlets in this series are of kindred interest:

- A.1. Magnetism and Electricity.
- A.2. Primary Batteries.
- G.2. Power Plant for Telegraph and Telephone purposes.
- G.3. Maintenance of Power Plant.
- G.4. Telegraph Battery Power Distribution Boards.

The following are also of interest:

- "Secondary Cell Maintenance and Records," Circular Telephones, June, 1919.
- Instructions on Telephone and Telegraph Secondary Cell
 Maintenance Procedure in the Secondary Cell.
 Log Book T.E. 1122.

MAINTENANCE OF SECONDARY CELLS.

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MAINTENANCE OF SECONDARY CELLS.

Probably the best way to understand a secondary cell is to make up a small one and to observe what takes place at the

various stages of the process.

The materials needed are of a simple character and are readily obtainable. The results obtained may not be quite the same numerically as in the examples which are assumed in the following description, but the proportions will hold good and there should not be any misunderstanding owing to the possible differences.

1. CONSTRUCTION OF SECONDARY CELLS.

To construct a secondary cell pour a quantity of diluted sulphuric acid in a glass or earthenware jar. Place two clean strips of ordinary sheet lead, which do not touch each other, in the sulphuric acid, allowing the ends of the strips to project. Connect the projecting ends of the lead strips by means of two pieces of wire to the 5-volt coil of the P.O. Detector No. 2. Observe that there is no deflection. Disconnect the wires from the Detector and connect them to two or three Leclanché cells joined in series. Allow the current from the Leclanché cells to pass through the circuit for a few minutes. Notice that the lead strip connected with the wire which is joined to the positive end of the Leclanché battery gradually becomes coated with a reddish substance whilst the other strip is apparently unaffected. Now disconnect the wires from the Leclanché battery and connect them to the 5-volt coil of the Detector. Observe that the Detector indicates, approximately, 2 volts immediately the circuit is joined up, but that after a short time the deflection gradually diminishes until, for all practical purposes, it becomes nil.

Again connect the lead strip with the Leclanché battery (taking care to join the strip which has turned a reddish colour to the positive end of the battery as before) and again allow the current to pass through the circuit for a few minutes. Then repeat the test by means of the Detector. Observe that the Detector again indicates about 2 volts and, further, that it takes a longer time than before for the deflection to diminish to the vanishing point. If this series of operations is repeated a large number of times it will ultimately be found that the cell will be capable of maintaining the deflection of 2 volts on the Detector for a considerable time.

Finally, the stage would be reached when it would be found necessary, in order to get maximum results, to leave the Leclanché battery connected to the lead strips for several hours to "charge" the cell fully, and that, on connecting the cell to the Detector for the purpose of "discharging" the

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cell, it would take a correspondingly long time before the

voltage fell much below 2.

The operation of charge and discharge repeated until the above mentioned stage has been reached is known as the "forming" process.

The condition of the elements of the cell on conclusion of

the forming process would be as follows:--

(1) On completion of a full charge:—

One of the strips, *i.e.*, the positive plate would be black.

The other strip, i.e., the negative plate would be lead coloured and have a somewhat porous appearance.

(2) On completion of a discharge :-

The positive plate would be a light red.

The negative plate would be grey in colour.

If the volume of dilute sulphuric acid used were small in relation to the size of the plates the changes in strength of the acid solution would, during the charge and discharge, be appreciable. It would be stronger acid at the beginning than at the end of the discharge, and it would regain its full strength at the end of the charge.

There would, then, be three distinct features by means of which one could, without actually discharging the cell, ascertain whether it was in a charged or a discharged condition,

viz. :--

(i) The voltage.

(ii) The colour of the positive plate, and

(iii) The strength of the electrolyte, i.e., the sulphuric acid.

These three features will be discussed later.

2. GASSING CHARGE.

Pursuing the investigations into the behaviour of the cell we should find that on applying the charging current to the discharged cell nothing would be observed to happen for a time inside the cell other than the gradual darkening of the positive plate. After a time, however, bubbles of gas would be seen to collect on the surfaces of both plates. Later on, the accumulation of gas would become so great that the bubbles would rise to the surface of the electrolyte in a steady stream. If the strength of the charging current is varied the stream of gas will vary—increasing when the current is increased and vice versa.

The presence of the gas gives a milky appearance to the electrolyte. Hence the expressions "Milking the cell" and

"Gassing the plates."

3. AMPERE-HOUR CAPACITY.

Assuming the cell to be used to light a lamp which requires I ampère, and that the cell would keep the lamp alight continuously for one hour before the cell had to be recharged, the

electrical capability of the cell would be stated to be such that it would yield a current of 1 ampère for 1 hour. If we changed the lamp for one which required $\frac{1}{2}$ ampère to light it we should find that the cell would maintain the lamp alight for three hours, and if we used a lamp which required $\frac{1}{4}$ of an ampère to light it the cell would be capable of keeping the lamp alight continuously for 8 hours.

The term ampère-hours means Ampères multiplied by

Hours.

Compare the ampère-hours in the three examples given:—

(a) I ampère x I hour = I ampère-hour.

(b) $\frac{1}{2}$,, \times 3 hours = $1\frac{1}{2}$

(c) $\frac{1}{4}$,, \times 8 hours == 2 ,,

Thus we see the ampère-hour capacity of the cell increases as the current used is reduced and, further, that in stating the ampère-hour capacity of the cell we must also state the current corresponding to that capacity.

The more usual way of connecting the ampère-hour capacity with the current is to express the latter in terms of the hourly rate. Thus, in the three examples given, it would be said

that the capacity of the cell is in:-

(a) I ampère-hour at a I hour rate.

(b) $1\frac{1}{2}$, hours , 3 , & (c) 2 , , , , 8 , .

If, therefore, we desire to know what the actual value of the current is at any hourly rate specified, all that is necessary is to divide the corresponding ampère-hour capacity by the hourly rate of discharge. In example (c), for instance, the current would be 2 divided by $8 = \frac{1}{4}$ of an ampère.

Consider now the conditions which determine the ampèrehour capacity of the cell at a given rate of discharge. When the cell is being charged the effect of the current is to bring about certain chemical changes in the elements, and when the cell is discharging the elements revert to the condition they were

in before the charging current was applied.

Assuming that the cell has an ampère-hour capacity of 2 at the 8-hour rate, and that it is in a discharged condition, recharge the cell by connecting it to the Leclanché battery through an adjustable resistance and a milliamperemeter, and join the 5-volt coil of the Detector No. 2 straight across the two lead strips. Adjust the current to \(\frac{1}{4}\) ampère and keep it steady at that value by adjusting the resistance.

The Detector will indicate a voltage of about 2.2. During the first part of the charging period the deflection will remain practically steady. About the sixth hour the deflection will slowly increase to a value approaching 2.7 volts. The voltage will remain perfectly steady at the value reached provided the current is kept constant, irrespective of the length of time the charge is maintained.

If the cell is carefully watched it will be seen that the plates begin to gas slightly at about the sixth hour, and that the quantity of gas formed increases gradually until a limit is

reached at about the eighth hour.

Stop the charge at the eighth hour. Now discharge the cell. To do this, merely disconnect the wires from the Leclanché battery and join them together, and then reverse the two wires on the milliamperemeter. Adjust the current to \(\frac{1}{4} \) ampère and maintain it at that value throughout the discharge. The Detector should remain connected across the cell. Observe that the voltage indicated by the deflection on the Detector remains practically steady until about the sixth hour, when it begins to decrease very slowly at first and then with increasing rapidity as the cell reaches the discharged stage, which, in ordinary circumstances, will be at about the eighth hour from the time of commencing the discharge. Thus, the cell has been charged with \(\frac{1}{4} \) ampère for 8 hours, and has been discharged at the same rate for very nearly the same period.

If the cell be re-charged at $\frac{1}{4}$ ampère for, say, 100 hours and then discharged at $\frac{1}{4}$ ampère, the cell would fail at the eighth hour as before, and it would be seen that nothing would have been gained by the prolonged charge. In fact, current sufficient to charge the cell many times over would have been wasted.

Again charge the cell at \(\frac{1}{4}\) ampère, but this time stop the charge at the fourth hour. On discharging the cell at the same rate, it would be found to fail about the fourth hour.

We therefore gather from these examples (1) that we cannot get more out of the cell than is put into it; (2) that the full ampère-hour capacity cannot be realised unless the cell be first fully charged; and (3) that waste takes place if the cell is charged for too long a period. Therefore, the importance of being able to determine when a cell is fully charged, and, for obvious reasons, when it is very nearly discharged, will be apparent.

4. SPECIFIC GRAVITY TESTS.

It can readily be shown, by means of the Detector No. 2, that voltmeter tests may easily lead to a serious misunderstanding. For instance, put the cell on discharge through the adjustable resistance at $\frac{1}{4}$ ampère and connect the 5-volt coil of the Detector No. 2 across the lead strips in the cell; note the voltage indicated by the detector. Allow the cell to discharge to the extent of about 95 per cent. of the ampère-hour capacity, then note the voltage indicated by the detector. This will be about 1.84 volts. Now reduce the current by inserting more resistance in series with the cell. Observe that as the current is reduced the voltage indicated is greater until, when the current is reduced to a very small value, the voltage indicated increases to 2 or very nearly so. But it has already been shown that the voltage of the cell when well charged up is 2. Therefore, before the

voltage reading can be relied upon for the purpose of judging the electrical condition of the cell, it is necessary to know the relationship between voltage and the discharge current for different values of each.

A second way of judging the electrical condition of the cell is by the colour of the positive plate. But this needs considerable practice, and there are several circumstances which may arise in practice which cause the colour to be affected and which might mislead.

There is still the third way of obtaining the desired information, *i.e.*, by observing the changes in the strength of the sulphuric acid, as will be indicated by measuring its "Specific Gravity"

by means of a hydrometer.

Specific gravity is the ratio between the weight of equal volumes of a substance and water. For example, suppose a quantity of water in a jug weighed exactly 1 lb. If we replaced the water by a quantity of dilute sulphuric acid (taking care to fill the jug to precisely the same level as when the jug contained water), and we found that the weight of the sulphuric acid was $1\frac{1}{4}$ lbs., we should say that for equal volumes of water and dilute sulphuric acid, the latter is heavier and must therefore be denser in the proportion of $1\frac{1}{4}$ to 1, or, to state it in decimals, 1.25 to 1. Seeing that water is taken as a standard, we could shorten the statement by saying that the relative density of the acid is 1.25, or that its "Specific Gravity," which is merely another term for expressing the relative density, is 1.25.

If in the water we placed a thin glass tube so weighted as to cause it to float vertically with a part of the tube projecting out of the water, and we marked the tube exactly at the water level and then transferred the tube to the dilute sulphuric acid, we should find that it would not sink quite so far in the acid as it did in the water. We could therefore put another mark on the tube corresponding with the level of the acid mark. If we placed the tube in any other fluid, we could at once see by comparing positions of two marks with the level of the fluid what the specific gravity of the fluid was in relation to water, for if the tube sank so that the water mark was covered, the fluid would have a less specific gravity than water, and if the tube did not sink to the level of the 1.25 sulphuric acid mark, the specific gravity of the fluid would be greater than 1.25. The tube is a hydrometer in an elementary form.

It has already been stated that the electrolyte in the secondary cell increases in strength when the cell is being charged, and decreases in strength as the cell is being discharged. In other words, its specific gravity increases on charge and decreases on discharge. If, therefore, we placed a hydrometer in the cell, the instrument would give a visible indication of the changes in the specific gravity of the electrolyte, and we should find that the changes were regular.

For example: Assume that the hydrometer shows that the specific gravity of the electrolyte when the cell is discharged is 1.185, and that it shows 1.205 when the cell has been fully charged. The change in specific gravity is therefore the difference between the two readings, thus:—

When the cell is being discharged the specific gravity of the electrolyte will be observed to fall from its maximum value 1.205 to 1.185 when fully discharged, the change again being .020.

Thus in this particular case the change of specific gravity is .020 for a full charge or discharge. Now this value is easily read on a modern hydrometer. It represents a length of the stem of the hydrometer of about $1\frac{1}{2}$ in., and it is easy to divide that length into 20 parts or divisions. In order to avoid having to use the awkward numbers the change of .020 would be referred to in practice as 20 hydrometer divisions.

We assumed that the cell had an ampère-hour capacity of 2 at an 8-hour rate of discharge. So therefore we could say with regard to this cell that 20 hydrometer divisions represents

a discharge of 2 ampère-hours.

It can readily be proved by trials with the cell that if it be only half discharged the change in specific gravity would be half the total change of specific gravity, or 10 hydrometer divisions, and it may generally be taken that in ordinary circumstances the change in specific gravity is directly proportional to the discharge in ampère-hours. Consequently if the full range be 20 hydrometer divisions, and, on inspecting the hydrometer we see that it is 5 divisions below the maximum specific gravity, we know that $5/20 \times 2$ amp. hours, i.e., $\frac{1}{2}$ an ampère-hour has already been discharged, and that there remains $15/20 \times 2 = 1.5$ ampère-hours still to be discharged before the cell will fail.

It does not matter whether the cell be discharged continuously or intermittently, the hydrometer will afford the means of determining the electrical state of the cell. Indeed, the hydrometer will give us more information than we can obtain by

relying upon an ammeter record.

Suppose the cell is lying idle, and by accident the two plates become more or less short circuited by some substance lodging between the plates. The cell will discharge through the short circuit, and the fact will be shown by the hydrometer readings. Again, suppose the electrolyte became contaminated by some means, for instance ammonia gas from Leclanché cells will alter the character of the electrolyte, and will cause the cell to become defective, the hydrometer will indicate that something is wrong by its irregular behaviour.

We have assumed that the total change in specific gravity in the cell we are considering is 20 hydrometer divisions. If we used the same plates in a different volume of electrolyte the change would not be 20 divisions, it would be more or

less according as we used a smaller or greater volume of electrolyte. Provided the range of specific gravity does not exceed about 50 hydrometer divisions, and the specific gravity does not fall below about 1.150 when the cell is discharged, the amount of electrolyte we use will not appreciably affect the ampère-hour capacity of the cell, and in practice it would not matter whether a change of specific gravity of, say, 25 divisions occurred anywhere between, say, 1.150 as the minimum and 1.230 as the maximum. In other words the cell would discharge 2 ampère-hours with the hydrometer range of 1.230 to 1.210 and, approximately, the same if it worked between 1.170 and 1.150, consequently the mere fact that a hydrometer reading is 1.200 is of no importance unless we know the normal range of gravity for the cell, the highest and lowest readings for a full discharge, and the relationship between the ampère-hour capacity and the specific gravity This must be determined by actual tests for each different size of cell.

5. MULTIPLE PLATE CELLS.

It will be observed that nothing we have yet considered has been the means of enabling us to increase the ampère-hour capacity of the cell beyond the assumed figure of 2 ampèrehours.

If we wanted to do this we should have to increase the size of the plates. If we doubled the size we should double the ampère-hour capacity. Then, in order to discharge the cell at the 8-hour rate we should have to adjust the current to a

value of $\frac{4 \text{ (ampère-hours)}}{8 \text{ (hours)}} = \frac{1}{2} \text{ ampère.}$

By "Size" is implied area multiplied by thickness. Now the ampère-hour capacity is influenced more by the area of the plates than by the thickness because the chemical action can readily take place all over the surface of a plate whereas it is not possible for it to penetrate much below the surface of the plate. If, therefore, we desire to increase the ampère-hour capacity of the plates in the cell we are considering we can do so by beating the lead out to a greater area, or we could achieve the same result by perforating the lead with a large number of small holes thus exposing a large surface to chemical action.

There is scarcely any limit to the size of a secondary cell and, therefore, to the ampère-hour capacity attainable. It is a question of size of plates. In practice the size of a single pair of plates to yield a large ampère-hour capacity soon becomes so great as to be inconvenient and, therefore, the plates are divided up into sections, all the positive plates being placed in one group and all the negative plates in another. They are

then interleaved in the electrolyte and kept apart by means of glass tubes, ebonite rods, or wood diaphragms. Theoretically there is no difference between the small cell we have considered and the largest secondary cell used by the Post Office.

Typical Cell.—Examine a typical secondary cell as used for a telephone exchange, for instance, and note the reddish positive plates and the grey negative plates. The reddish colour of the positive plates may be somewhat obscured by a loose whitish deposit which can be readily brushed off. Observe how the maker of the cell has endeavoured to procure the maximum surface area on both sets of plates. extra negative plate and that the negative plates are thinner than the positive plates in order to compensate for the extra negative plate. The reason for the extra negative plate is seen by considering a two-plate cell and a three-plate cell. With a two-plate cell there are two surfaces out of the four facing each other and the current has to travel a comparatively long distance before if affects the outer surface. With the threeplate cell there are four surfaces out of six very close together, and there is therefore a gain in the effective spacing of the plates. The relatively close spacing of the plates and the nature of the materials used result in the cell having an exceedingly low internal resistance.

6.—CAUSES OF FAILURE.

In practice, cells which are properly treated fail normally owing to positive plates wearing away until they become too weak to hold together, or by the negative plates losing their porosity. They are also liable to fail prematurely as the result of defective treatment.

Buckling.—Positive plates are liable to twist or buckle and the cause generally is uneven chemical action on the plates. This in most cases is the result of discharging for too long

a period or not charging the cell sufficiently.

If the full ampère-hour capacity is not made use of, or, if the cell be allowed to remain in a discharged or partly discharged condition for a long period, the sulphuric acid will, by slowly attacking the lead, cause a white substance to form on the surface of the plates. The substance is lead sulphate and a plate on which the substance has formed is referred to as having "sulphated." The lead sulphate is a very bad conductor of electricity.

If therefore, we consider a plate which has been attacked, and of which a part of the surface has become covered with the white sulphate, that part of the plate will become inert. Now the normal chemical changes which take place in the plates as the cell is being charged and discharged cause the plates to expand and contract alternately and so long as they do this uniformly there is no difficulty. If, however, a portion of a plate be rendered

ineffective, distortion is likely to take place. Moreover if a slight distortion occurs the spacing between plates will become uneven and the distortion will tend to increase as time goes on

until ultimately the plates become short circuited.

If we examine a cell which has been in use for a year or two we shall observe that the plates are not quite square. If they have had space in which to expand freely they will do so. The probable explanation of this is that in virtue of the ductile nature of lead it expands readily but does not so readily regain its original shape. Consequently in the cycles of expansion and contraction the former has a permanent influence and the plates "grow." This permanent expansion must be allowed for, otherwise, if the space be restricted the plates will buckle. It is necessary to control the distortion only when it takes place at the bottom of the plate in the direction at right angles to the plane of the plate. The bent lead strips or "Lead springs" as they are called which are frequently placed between the end plates and the inner sides of the containing vessel exert sufficient pressure upon the plates to prevent them bending outwards.

Impurities.—A frequent cause of failure in a secondary cell is the presence of impurities in the electrolyte. In general, the effect of an impurity is to cause the cell to discharge itself internally. Even a mere trace of a foreign substance such as iron, manganese, gold, copper, etc., is sufficient to cause difficulty. Ammonia gas has already been referred to. Water which is perfectly suitable for drinking purposes will in most cases be harmful to a secondary cell. Commercial sulphuric acid, or B.O.V. acid, as it is called, is altogether unsuitable.

There are several other points in connection with the maintenance of secondary cells which could be touched upon, but it is thought that sufficient has been said to enable one to understand the general principles which underlie the standard instructions and notes for maintaining secondary cells and the keeping of the records. These are included in the present standard secondary cell log book, and were also issued with the

monthly list for June, 1919.

P.W.-G.1.

Page 11. After Altogether unsuitable insert the following:-

7. TOPPING UP.

The best electrolyte for lead plate secondary cells is dilute sulphuric acid of a specific gravity of 1.215. Strong sulphuric acid has a specific gravity of about 1.84. freely exposed the strong acid will absorb moisture from the atmosphere and will continue to do so until the acid attains a specific gravity of about 1.4. At that stage a certain amount of the moisture which has been absorbed by the acid will, on a hot dry day, be returned to the atmosphere and will be re-absorbed when the air is colder or more moist. Weaker acid will evince a greater tendency to get rid of the water it contains until the acid reaches the critical specific gravity value of 1.4. sequently the volume of exposed electrolyte in a secondary cell becomes less and less as time goes on, owing to the continuous loss of water by evaporation. The acid will become denser and pure distilled water must be added to restore the electrolyte to its original condition and volume.

A certain amount of the electrolyte (i.e., the acid and the water) is also lost by spraying, but the amount is negligible compared with the quantity of water lost by evaporation. Nevertheless, it is the finely divided spray thrown up by a cell on charge that mixes with the air and causes the choking smell so plainly observable in a badly ventilated battery room, and tends to corrode any metal fittings which may be surrounded by the acid laden air.

It has recently been found that the evaporation of the water can be practically prevented and that spraying and fumes are eliminated if a thin layer of pure petroleum oil, "oil, insulating, No. 3," be poured over the exposed surface of the electrolyte. If any other kind of oil be used, there is a danger of its being attacked by the acid and gases and substances being formed which may be harmful to the cells.

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(Continued.)

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