# THE INSTITUTION OF POST OFFICE ELECTRICAL ENGINEERS

# SECONDARY CELLS

(LEAD-ACID TYPE).

BY

H. M. TURNER.

## A PAPER

Read before the South Lancs. Centre of the Institution on the 10th December, 1928, and before the N. Ireland Centre on the 8th April, 1930.

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# SECONDARY CELLS (LEAD-ACID TYPE).

#### Introduction.

The increasing use of Secondary Cells of the lead-acid type for telephone and telegraph purposes by the Post Office Engineering Department, together with recent improvements in design, manufacture and maintenance methods will, it is hoped, render acceptable a paper embodying the most recent information in this subject. The paper is divided roughly into two sections, the first dealing with the chemical and physical properties of cells, and the second with their maintenance.

The plates of a secondary cell are of two distinct types, Planté and Pasted or Faure. Both types are used for positives, but the Planté negative plate is now obsolete. The Box type of negative is a special form of the Pasted type.

#### Pasted Plates.

In this type the active material is held in a grid which is a lead-antimony alloy containing about 7% of antimony. The presence of the antimony not only increases very considerably the strength of the grid, but also reduces the corroding action of the acid, and thereby lengthens the life of the plate. The grid of the positive plate plays an important part in conducting the electric current, since the electrical resistance of the paste in the form of lead peroxide is 300,000 times that of pure lead. Uniform current distribution is essential for long life.

The paste may be made from practically any oxide of lead. Litharge is mainly used for negatives as it is easily obtained, and, since it contains the least amount of oxygen to be liberated in the forming process, the forming time is reduced to a minimum. Similarly red lead is mainly used for positives since the amount of oxygen to be absorbed is a minimum. Various ingredients are added to the paste during manufacture. The paste may be hardened or stiffened by the addition of glycerin. Other materials added are called porosity agents: these dissolve out during the forming process and leave the paste porous. Sugar may be used for this purpose.

Finally, other materials, called expanders are added to the negative paste. During the life of a negative plate, the sponge lead, which is the active material, contracts and by exposing a smaller surface area to the action of the acid reduces its capacity very considerably. Powdered substances which are insoluble in acid, such as lamp black, graphite, pumice, porcelain and barium sulphate introduced into the sponge lead, restrict, to a very considerable extent, the contraction and loss of capacity. The employment of an excessive amount of expander tends, however, to force the active material out of the grid and the exact quantity introduced requires careful determination.

The pasted plate when finished should neither be too hard nor too soft. Hard plates are of low capacity and suffer from sulphation if left even for a short time, while soft plates have a short life.

In the forming process the positives and negatives are usually formed against one another in a dilute sulphuric acid solution.

Pasted positive plates lose active material in service by shedding, and the capacity is maintained so long as there is sufficient active material left in the grid. Shedding should not begin until after 60 to 70 cycles. Pasted negative plates wear in service by shrinkage of the active material which causes it to become less porous and therefore to lose capacity.

#### Planté Plates.

The Planté type of plate is formed by pouring the molten lead into a mould, the flat surfaces of which are deeply indented with parallel narrow V shaped grooves, so that the plate surface consists of a series of thin leaves or "lamelles" which present an area of from 6 to 8 times the dimensional area of the plate to the action of the acid.

This surface is formed into a film of lead peroxide between 1/64" and 1/32" in thickness, and it is this film only which enters into chemical action, the main body of the lead plate being the reserve mass of lead which is drawn upon during the working life.

The Demi-Planté plate has a less highly developed surface than the proper Planté plate, but the space between the lamelles is filled with active paste. When the plate is new, it functions as a pasted plate, but as the paste sheds it becomes more and more a Planté plate in its action.

The process of forming a Planté plate is much longer than that of a pasted plate. The positive plate is first formed against lead-antimony dummies in a solution of sulphuric and nitric acids. The surface of the plate is attacked and formed into lead peroxide. In the second stage, the positives are charged in the opposite direction in a sulphuric acid solution and spongy lead formed. The plates are then thoroughly washed and charged in the original direction, the surface being converted again to peroxide. The object of the last two stages is to remove the traces of the forming agent, *i.e.*, nitric acid, or similar agent. Over-formation gives the plate a high capacity, but reduces the reserve of lead in the plate to such an extent that the life is very considerably shortened.

Planté positive plates wear in service by shedding their active material, and as fast as this occurs, new lead is automatically corroded and formed to lead peroxide, at the expense of the original reserve of metallic lead in the plate. The life of the plate is at an end when the lead becomes so corroded that the plate is mechanically weak. Planté plates expand during their life and they are designed to concentrate this expansion in a downward direction as far as possible, since lateral expansion leads to the buckling of the plate or bursting of the container. Normally, a Planté positive expands in a downward direction about 5% of its length during the course of its life.

Pasted and Planté plates each have their advantages and drawbacks. Pasted plates are used for slow discharge rates, but they may be used satisfactorily for high discharge rates over short periods. Planté plates are more suitable for normal discharge rates over long periods. American practice is to use pasted plates for stand-by batteries in central stations partly because of their high output for weight, but also because they can be allowed to stand for longer periods without charging than Planté plates. Local action between the positive active material and the lead base is much less with the solid mass of active material on the pasted plate than on the large developed surface of the Planté plate. A pasted plate will give about 21 times the capacity in emergencies that a Planté plate of the same size will give. Planté plates are heavier, bulkier, and cost more than pasted plates for the same capacity; on the other hand they give a longer life.

# Box Negatives.

These are a special form of pasted or Faure plate in which the active paste in the form of pellets is enclosed in a grid which has on each face a perforated lead sheet. This form allows free access of the electrolyte to the paste and enables a much more porous paste to be used than is possible with a pasted plate. They, therefore, retain their capacity over a large number of years.

# Chemical Theory.

The general theory of the secondary cell is familiar to all and space will not permit of any detailed consideration of the chemical reactions which take place. The theory put forward by Gladstone and Tribe in 1882 is, in spite of opposition, still held to be correct. This is the double-sulphate theory which states that lead sulphate is formed on both plates on discharge. On charge, the negative paste is converted to spongy lead and the positive active material to lead peroxide. The chemical equation on discharge is given below:—

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Positive. Electrolyte Negative. Positive. Electrolyte. Negative. PbO<sub>2</sub> + 2H<sub>2</sub>SO<sub>4</sub> + Pb = PbSO<sub>4</sub> + 2H<sub>2</sub>O + PbSO<sub>4</sub>
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In 1917 Féry suggested that since the colour of a charged positive is black rather than chocolate, the active material was a higher oxide than lead peroxide, and on a similar argument that the discharged negative was the dull grey Pb<sub>2</sub>SO<sub>4</sub> rather than the white sulphate PbSO<sub>4</sub>. Measurements made in 1927 showed that the theory of Féry was not correct.\* The average composition of a charged positive plate is†:—

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Lead Peroxide ... PbO<sub>2</sub> = 90\%
Lead Oxide ... PbO = 7\%
Lead Sulphate ... PbSO<sub>1</sub> = 3\%
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The composition of a negative plate is:—

Lead Oxide ... PbO = 3%Lead Sulphate ... PbSO<sub>4</sub> = 2%Lead (spongy) ... Pb = 95%

<sup>\*</sup> Revue Générale de l'Electricité, Jan., 1917, and Jan., 1927.

<sup>+ &</sup>quot;Storage Batteries," G. W. Vinal, 1924.

These values are approximate and vary with different plates and conditions. An important feature of the above figures is the 3% of lead sulphate which remains on a charged positive plate. This is not easily removed by excess charging and is actually of considerable importance in acting as a binder of the active material.

# Physical Characteristics.

The capacity of a cell depends upon a very large number of factors, such as concentration of the electrolyte, temperature and discharge rate. Dealing first with the electrolyte, the internal resistance of a cell should be a minimum for high capacity and since the whole of the current passes through the electrolyte, the resistance of the electrolyte should be a minimum. Now the resistance of sulphuric acid varies very greatly with the degree of concentration and is a minimum tor a specific gravity of about 1.220. (See Table II., Appendix). For this reason this figure is adopted as the upper level in telephone batteries. The limits of range of specific gravity for stationary secondary cells are 1.170 and 1.210. The density of the electrolyte in the cell is not, in general, the density where it is in intimate contact with the active material. When a cell is put on charge, the electrolyte that is locked up in the pores or lamelles of the plates becomes more concentrated and increases in gravity and this increase is transmitted by diffusion throughout the electrolyte. This explains why there is no apparent gravity rise for about an hour after a cell is put on charge. Similarly at the end of the charge, the high density acid locked up in the pores gradually diffuses and the specific gravity as shown by test may rise three points or more after the charge is cut off.

The capacity of a cell depends very largely upon the rate at which any gravity change is diffused throughout the electrolyte. The low capacity of a cell at a high discharge rate is due solely to the fact that there is insufficient time for satisfactory diffusion. The average voltage on discharge depends very largely upon the diffusing property of the electrolyte. The most nearly flat characteristic is obtained by wide separation of the plates, abundance of electrolyte and relatively low discharge rates.

Temperature has a very large influence upon the capacity of a cell. Increasing the temperature causes an increase in the capacity, due to three causes:—(1) The resistance of the

electrolyte decreases as the temperature rises. (2) The voltage is raised with temperature increase. (3) The rate of diffusion of the electrolyte is increased. The last is the chief cause. The percentage increase in capacity for each degree rise of temperature (Fahr) varies with the discharge rate and is about one half of one per cent. at the 9-hour rate.

The capacity varies with the life of a plate, increasing after a few cycles to a maximum value and then falling off. The maximum capacity in the case of thin plates is reached sooner than with thick plates. The life of a plate is proportional to its thickness. The best value (taking capacity and life into account) for the thickness is 12 m.m. or just under  $\frac{1}{2}$ ", and this size has been standardised in the Post Office for all except the smallest and largest size of plates. For various reasons connected with the strength and weight of the plate the thickness of the largest plates has been reduced to 10.5 m.m.

# Engineering Applications.

Secondary cells are divided broadly into two classes:—
(1) Stationary types and (2) Portable or Vehicle or Traction types. Space does not permit of detailed description of various types, and treatment will be limited to special features of the standard types of stationary cells used by the P.O. and a general description of vehicle batteries.

# Stationary Cells.

The smaller sizes of cells have been standardised for a considerable time and the various sizes and capacities are fairly well known. Eleven sizes are used, giving capacities from 8 to 300 amp.-hrs. The positive plates may be either of the pasted or Planté or demi-Planté type, while the negatives may be either pasted or of the Box type.

The standardisation of the larger sizes of cells, from 400 amp.-hrs. to 13,800 amp.-hrs. is a very large step forward in battery use and has been completed successfully recently. The positive and negative plates are assembled in groups of 2 or 3 sections and 2, 3, or 4 sections, respectively. The groups are fitted with lugs for connection by bolts and any capacity of cell may be made up by a suitable assembly of these groups.

The advantages of the group system of assembly are: -

- (1) Repairs may be undertaken without the assistance of staff skilled in lead burning.
- (2) Repairs may be carried out, if necessary, on a discharging battery.
- (3) Inspection of the plates is simplified.
- (4) Re-arrangements of plates for extension of capacity is simplified.

The chief point to be observed in the assembly of the groups is that the contact surfaces are quite clean. They must, after separation, be well scrubbed with a file-card and covered with petroleum jelly before bolting together. The surfaces are pulled together with a steel bolt and then the connection bolt is inserted and pulled up. If the joint is satisfactory, the total resistance will be negligible. In practice, the contact at the faces is so good, that, to force them apart, it is sometimes necessary to use wedges. The individual groups of plates in the same cell are interconnected with leadized copper straps or bus-bars.

#### Separators.

Except for the smallest cells glass tube separators have been standardised by the Post Office, the use of wood separators being abandoned. The chief reason for this is that for satisfactory working a telephone battery must have a low internal resistance. In order to compare the relative resistances of cells with various types of separation, it is necessary to reduce the distance apart or separation of the plates to a standard value. If this separation be ½", the internal resistance of a fully charged secondary cell (without separators) is given approximately by the formula:—

Resistance =  $\frac{0.25}{\text{Amp-hour capacity}}$  Ohms. The resistance of a cell when discharged may be twice its resistance when charged. Measurements show that for the same plate separation, the resistance of a wood-separated battery is about twice that of a glass-tube separated battery. Wood separators have the advantage of preventing small short-circuits due to "tree" formation, but on the other hand, it is practically impossible to remove a wood separator from a cell even if the plates are buckled only slightly.

# Anti-spray Oil Film.

Pure paraffin oil is used for covering the surface of the electrolyte. The practice was introduced in the Department in 1921 and is now standard. The advantages claimed for it are:—

- (1) Reduction in consumption of distilled water.
- (2) Special ventilation is not required for battery-rooms.
- (3) It enables apparatus to be placed in the same rooms as the batteries in unattended exchanges.
- (4) It enables rooms to be used as battery rooms which would otherwise be unsuitable.

Its chief disadvantage lies in the fact that when carbon is used as an expander freed carbon rises into the oil and forms a thick black mass, preventing the plates from being seen and rendering taking of correct hydrometer readings a matter of difficulty. Plate design should, therefore, be such as to avoid excess of carbon expander.

#### Vehicle Cells.

A short space will be devoted to the main features of vehicle or traction cells and the chief points on which they differ from stationary type cells. These cells are destined to play a much larger part in transport than hitherto now that their sphere of utility has been realised. The early attempts at the use of secondary cells for traction work failed from a variety of causes, some quite unconnected with the cells themselves, and as a result it is only during the last few years that the prejudice against their use has been overcome.

Since weight and bulk are considerations of great importance, the pasted or Faure plate is most commonly used, as this possesses the highest capacity-to-weight ratio. Apart from the container, which, in the vehicle battery, is moulded ebonite or a substitute, the chief difference between the portable and stationary types lies in the method of separation. Wood sheet separators are commonly used, but the glass-wool separator has recently come into greater favour. It is made from spun glass-wool in sheet form and in appearance very much resembles a porous pasteboard. Its advantages are:—

- (1) It effectively retains the active material in the grids.
- (2) It allows free circulation of the acid.
- (3) It allows free escape of gas.
- (4) It is elastic and, being under slight compression, prevents any movement of the plates.

With this construction practically no sediment is thrown down and the disadvantage of the pasted plate, *i.e.*, shedding, disappears.

Another type of vehicle cell is one in which the active paste is contained in thin ebonite tubes perforated with small slits throughout their length.

A particular form of traction cell is the "submarine" cell and a comparison between this type and a stationary cell of similar capacity is given below:—

	Stationary type.	Submarine type.
Capacity at 9-hr.		••
rate	3,800 A.H.	4,100 A.H.
Weight	2,000 lbs.	920 lbs.
Dimensions	$40'' \times 19' \times 39''$ high.	$17'' \times 13\frac{1}{2}'' \times 44''$ high.
Watt-hrs. per lb.	3.6	8.4

The electric vehicle is particularly adapted for work in congested city areas with frequent starting and stopping and is cheaper than a petrol vehicle. Its limitation lies in its radius of action, which is about 30-35 miles per charge. Extensive use of electric vehicles for refuse collection and similar work has been made by large municipalities including Glasgow, Birmingham, Nottingham and Sheffield, the last named employing 75 vans on refuse-collecting alone. The American Express Co. employs a fleet of 2,000 electric vehicles. Electric vehicle manufacturers have concentrated too much in the past on the larger sizes of vehicles, about 3-4 tons, but small 1-ton and  $1\frac{1}{2}$ -ton vans are now being marketed and are unquestionably economical in their proper sphere.

For rail work the chief applications are for underground work including coal mines and for shunting locomotives. In the P.O. London Tube Railway three battery-driven locomotives are held in reserve at certain stations for the purpose of hauling any trains which have been brought to a standstill due to a failure of electric supply. Each of these locomotives is fitted with 163 cells of 84 amp.-hr. capacity: they were particularly useful during the latter stages of the construction

work. In the United States of America the largest battery locomotive in the world has recently been put into service. It weighs 110 tons and is capable of hauling a 1,500 ton train at from 8 to 10 miles per hour. The battery consists of 120 cells with a capacity of 616 k.w.h. and weighs 39 tons. This instance is mentioned as a remarkable illustration of the potentialities of battery traction. Two locomotives have recently been built in this country equipped with batteries developing 600 horse-power for starting under load.

#### Cadmium Test.

In addition to determining the capacity of secondary cells, it is sometimes necessary to ascertain the capacity of the positive and negative plates separately as a means of locating faults in the operation of the cells. This may be determined by the use of a constant auxiliary electrode immersed in the electrolyte of the cell.

The auxiliary electrode in most general use is the cadmium electrode. Its usual form is a stick 5/16" in diameter and two to three inches long, held in an ebonite holder and insulated throughout its length in such a way as to allow the electrolyte free access to its surface but to prevent contact with the plates. A flexible wire for connection is attached to the cadmium. Potential difference between the cadmium and either positive or negative plate is measured on a voltmeter placed in circuit with the electrode. Readings may be taken on charge or discharge, but open-circuit readings are valueless. Three precautions are necessary in using the electrode, if the readings are to be of any value:—

- (1) The cadmium should be soaked in the electrolyte for about one hour before use.
- (2) A high resistance voltmeter should be used.
- (3) The electrode should be placed as near to the centre of the cell as possible.

The difference of the cadmium-to-negative and cadmium-to-positive potentials is equal to the cell voltage.

On a discharging cell the most useful readings are obtained when the cell voltage is about 1.83 or less. Typical results to be expected are tabulated below for the sake of clearness.

# Cells discharged. Voltage 1.83.

Readings for cell in good condition:

Cadmium to Positive ... + 2.06 Cadmium to Negative ... + .23

Positive exhausted.

Voltage less than 1.83.

Cadmium to Positive ... less than + 2.0 volts. Cadmium to Negative ... + .23

Negative exhausted.

Voltage less than 1.83.

Cadmium to Positive ... + 2.06 Cadmium to Negative more than + .23 volts.

On charge the cadmium stick can be used to give valuable readings. Typical results are given below:—

# Cells charging.

Beginning of charge. Voltage 2.1.

Cadmium to Positive ... + 2.25 Cadmium to Negative ... + .15

End of charge. Voltage 2.6.

Cadmium to Positive ... ... + 2.45 Cadmium to Negative ... - .15

The cadmium-to-positive voltage rises evenly as the charge proceeds, but rather more rapidly at the end of the charge. The cadmium-to-negative reading gradually falls to zero just before the completion of the charge, and then reverses, and gives a small reading in the opposite direction when the cell is fully charged. This reversal does not always take place with old plates.

Owing to the unavoidable inequality in current distribution, among the plates, (and even over the area of the plates) considerable variation in cadmium readings will be obtained in different positions in the cell. It is for this reason that the cadmium stick should always be used in one position—the centre of the cell.

An important point should here be mentioned. When a low-resistance voltmeter is used with the electrode, the current may be sufficiently high to set up polarisation of the electrode. This polarisation is proportional to the potential measured and is therefore about 10 times as great when measuring the positive potential as when measuring the negative and may reach .1 volt in the case of the former. The resistance of the 5-volt scale of a Detector No. 4 is 500 ohms and the polarisation error is probably considerably less than .1 volt. If, however, any error is suspected, the best procedure is to measure the cadmium-to-negative potential and to obtain the cadmium-to-positive value by deducting from the cell voltage.

#### Maintenance.

A battery of secondary cells may be regarded from two entirely different view-points. Normally, each cell responds identically to external influence such as charging rates, etc., and each suffers in a similar manner from any maltreatment of the battery as a whole; but on the other hand, each cell is prone to troubles of its own which, if neglected, reduce the efficiency and utility of the battery as a whole. Troubles in batteries may be due to two causes:—Firstly, faulty methods of treatment, and, secondly, failure to attend to small troubles at an early stage. Dealing, firstly, with the faulty methods of treatment, the four given below are the commonest:—

(1) Overcharging. (2) Undercharging. (3) Overdischarging and (4) Underdischarging.

# Overcharging.

This is, perhaps, one of the most common forms of illtreatment and as the ill-effects are not immediately observable, the treatment is continued until such time as the cell collapses. As stated earlier, the depth of formation of active material on a positive plate is from 1/64" to 1/32" thick, and beneath that is pure lead. Now if we rubbed that surface off, we should have to form again and make another  $\tau/32''$  of active material. This rubbing or scouring action is produced by the gases which are developed towards the end of the charge. The active material which is rubbed off is deposited at the bottom of the box. Practically the whole of the removal of the active material takes place during the gassing period and is proportional to the amount of gas generated (which depends upon the charging rate) and also to the time during which gassing proceeds. Hence overcharging by charging for too long a period and charging at too high a rate during the gassing period both produce the same result, i.e., the scouring away of the active material, necessitating the further forming of the lead base.

It has already been mentioned that the life of the positive plate is at an end when the lead base is worn so thin that it cannot support its own weight, and the result of overcharging is merely that the plate is worn away at a much faster rate than should be the case. A certain amount of overcharging and gassing is necessary to ensure that all but 3% of the lead sulphate is formed into lead peroxide and the important question is at what point should it cease. One method is to work the battery at a fixed efficiency, *i.e.*, the charge to be given is calculated on the efficiency of the battery and the ampere-hours capacity taken out on the last discharge. This method has four disadvantages:—

- (1) The efficiency varies with the rates of charge and discharge.
- (2) The efficiency of all the cells may not be the same.
- (3) The efficiency of every battery would have to be obtained in the first instance.
- (4) Confusion results if the attendant has several batteries of different efficiencies to maintain.

By similar reasoning, the 10% overcharge which is often quoted as being correct, should not be used as anything more than a rough check.

The best method of control is by specific gravity. While a cell is being charged, the specific gravity rises steadily until the end of the charge. After that stage, if the charge is continued, the gravity will only rise very slowly, due to the decomposition of the water in the electrolyte causing the acid to become more concentrated. As soon as the charge is stopped, the more concentrated acid locked up in the interstices of the plates is released and diffuses and the gravity may rise two or three points during the next  $\frac{1}{2}$  hour or so. This lag in the gravity should be known for each battery by the attendant. It is clear, therefore, that the battery should be charged until the gravity is within the ascertained number of points of the top gravity. If there are any doubts as to exact " lag " of gravity, it is advisable to over-estimate it, as any undercharging will be made up for at the monthly overcharge.

There is a novel method, due to Capt. Lucas, of the Engineer-in-Chief's Office, whereby regular overcharging may be detected, and a description of this may be of value. During the gassing period some of the water in the electrolyte

is transformed into gases which escape into the atmosphere. The amount of water so lost cannot be measured, but the amount of distilled water that is replaced can be very easily ascertained. Now the amount of water evaporated with a 10% overcharge is given by the formula:—

where

A = average number of amp.-hours discharged between one charge and another.

N = number of cells in the battery.

D = number of discharges taken into account in the period.

This should equal the amount of water replaced. To illustrate this by a particular case:—At a certain telephone exchange with two 11-cell batteries of 2000 amp.-hours each and a 24-hour discharge of 1300 amp.-hours, 156 gallons of water were used in a year. Allowing 25% for spilling, etc., this gives 120 gallons put into the batteries. The batteries were charged every day and with a 10% overcharge, the annual consumption would be 32 gallons. The overcharge was, therefore, about four times this, or 40%. This amount of overcharge was verified by the examination of the log books. This formula assumes the presence of the standard oil film. If this is not present, water is lost by evaporation and spray and the loss is about  $3\frac{1}{2}$  times the calculated figure. The formula gives a useful check on overcharging and is not dependent upon the accuracy of any instrument. monetary loss due to overcharging is dealt with later.

Other effects of overcharging are:

- (1) The particles of active material rubbed off the positive plate are conveyed across the electrolyte and deposited on the negative plate where they produce growths known as "trees." These growths of spongy lead may become sufficiently large to bridge across and short-circuit the plates.
- (2) Violent gassing in the negative plate causes the paste to be blown through the small holes in the grid. This also produces short-circuits and ruins the negative plate.

(3) Buckling of the positives may be caused in time, as the excessive formation of peroxide occupies a greater volume than the lead forming the base or reserve.

# Undercharging.

This is often the result of extreme caution on the part of the attendant to avoid overcharging. Unlike the latter fault, the results are soon observable. The sulphate formed on discharge is converted to peroxide or reduced to lead on charge; if the charge is stopped too soon, some of the unconverted sulphate is left on the plates. If this undercharging is continued regularly, the unconverted sulphate will become obdurate and the battery loses capacity. Undercharging is generally more harmful to negatives than to positives, as the abnormal sulphate fills up the pores of the active paste. At the same time, however, the positive plates may buckle due to the expansion of the active material consequent upon the conversion of the lead peroxide into the more bulky lead sulphate. Another result of undercharging is that the protective film of oxide which is believed to exist between the skin of active material and the lead base of the positive plate is broken down by the lead sulphate and local action then takes place at such a rate that the plate soon becomes rotten and drops to pieces.

Early indication of undercharging is given by the steady fall of the top gravity reading even after the equalizing charge. The only cure is to prolong the charge at normal rate if the trouble is observed at an early stage, or at a lower rate if abnormal sulphate has formed.

Undercharging is also indicated by the white colour of the deposit at the bottom of the cell instead of the normal dark colour of the peroxide deposit. The white colour indicates the presence of abnormal lead sulphate. The plates will also be pale in colour.

# Overdischarging.

By this is meant discharging below the permissible voltage. After a certain capacity has been abstracted from a fully-charged cell, the terminal voltage will have fallen to a value which depends upon the rate of discharge. At this stage, a definite quantity of the active material of both plates will have been reduced to lead sulphate. The Post Office has

standardised the discharge rate of cells at the 9-hour rate and the minimum voltage corresponding to this rate is 1.83 volts. More capacity can be obtained from this cell by reducing more active material to sulphate, but for several reasons this is not desirable. Spongy lead and lead peroxide both expand considerably on being converted to lead sulphate; lead peroxide expands to nearly twice its previous volume, whilst spongy lead swells to nearly three times its volume. A definite weight of active material on both plates is reduced to sulphate for each amp.-hour discharged, independent of the rate, which means that the expansion of active material during discharge is proportional to the amp.-hours discharged. (See Table III., Appendix). The lead base or grid of the plates is designed to withstand a fixed amount of expansion and any further expansion beyond that point may distort and buckle the plates. Now the gravity range of the cell gives the true indication of the amp.-hour capacity and it is clear, therefore, that the limit of discharge is reached at the lowest figure of the gravity range. Any discharge obtained from the cell after that point has been reached causes permanent distortion of the plates. Regular overdischarging results in increasing distortion until the plates buckle.

There is an erroneous impression, which is quite commonly held, that so long as the battery voltage does not fall below the exchange standard, the discharge may be continued. This may mean the gravity falling below the lower limit and as the manufacturers only allow a slight margin on the plate design, the discharge should not be continued to the lowest voltage, but should cease at the end of the gravity range.

Apart from the buckling effect, another result of overdischarging is that at the lower gravities abnormal sulphate is formed in the pores of the negative plates and this results in the active surface being reduced, with consequent loss of capacity.

# Underdischarging.

It is a well-known feature of a secondary cell that if it is regularly discharged to the extent of only a fraction of its capacity, its actual capacity, in time, becomes reduced to that fraction. This is due to a number of causes, one of which is that the layer or skin of active material on the positive plate becomes thin due to lack of reduction and further formation. Provided the working limits are not exceeded, the life of a

secondary cell is dependent upon the number of discharges and not upon the extent. A cell will not give a longer life if discharged to only half its capacity than it will if discharged to its full capacity. The cell may give a slightly longer life, measured in years, if only half discharged, but the amperehours discharged during the whole of its life will be much less than it would be if the cell were fully discharged.

The discharge to be aimed at in telephone exchange working is 100%. If a battery with Planté plates has been discharged to, say, 90% of its capacity, the amount in hand for emergency is not 10%, but about 25%. This margin is due to two reasons:—

- (1) The battery makers design the plates to withstand a discharge at the 10-hour rate which is slightly greater than can be obtained at the 9-hour rate.
- (2) The capacity of the plate increases during the early part of its life, sometimes as much as 10%.

It should be clearly understood, however, that the use of this margin is only allowable for emergency and not for regular working. From this aspect, therefore, there is no reason why 100% working should not be aimed at. Again, there is no good reason why a battery which has been discharged 80% on a particular day, should not be kept in service to discharge the remaining 20% on the following morning. The battery may be safely left over-night and charged the next morning and it is left to the attendant to decide whether it is worth making use of the rest of the capacity next day. The loss which results from underdischarging a battery is the monetary loss of capital and interest represented by the undischarged capacity of the battery and in the case of large batteries may reach a formidable figure.

Another consideration affecting the treatment of the battery as a whole is the rate of charging. This may be at three rates:—(1) High. (2) Normal. (3) Low.

High-rate charging is often confused with overcharging. No harm is done to a cell by charging at a high rate so long as it is not gassing. High rate charging during the gassing stage produces violent gassing and therefore has the same result as overcharging. Until gassing begins (at about 2.45 volts per cell), the charging should be at the maximum output of the machine provided that it does not exceed twice the normal (9-hour) rate. It is more economical to run the charg-

ing machine at its full load than at any lower figure and apart from this fact a saving is effected by getting the largest part of the charge into the cells before the voltage rises.

# Low-rate charging.

If a cell is charged for a long period at a rate lower than one half its normal rate, a layer or skin of hard sulphate is formed over the surface of the active material of the positive plate which is very difficult to remove. Abnormal sulphate on a negative plate is, however, removed or softened by low-rate charging. The treatment of sulphated negatives involves charging at a low rate for a long period and in the process some slight damage is done to the positives. This is unavoidable, but may be rectified by later charging at a high rate, when the negatives are in condition. Low-rate charging is more destructive to Planté plates than to pasted plates (owing to the larger area) and does not injure negatives at all.

#### Low electrolyte level.

Dealing now with individual cell troubles, a common failing in battery maintenance is that the electrolyte is not topped up at frequent and regular intervals, and is therefore allowed to fall below the top edges of the plates. If the upper surfaces become exposed to the air, the reduced surface of the plates acted upon by the electrolyte becomes overworked and the life is thereby shortened. In addition, the water in the exposed part of the negative plate is evaporated and the remaining acid trapped in the pores of the active material becomes concentrated and converts the spongy lead to abnormal sulphate. Furthermore, if the electrolyte is only topped at long intervals when considerable electrochemical decomposition of water has taken place, the gravity readings are completely upset and some time must elapse before the conditions are normal.

## Internal Short-circuits.

These may be due to "trees" or growths on the negative plate, or to scale, or, in the case of some cells, to buckling. The presence of the first two is indicated on the first occasion when the gravity fails to rise to the normal reading. If the short-circuit is cleared as soon as possible no harm results, but generally short-circuits are not cleared as soon as desir-

able. In the case of a battery with burnt-up plates, if the short-circuit is not cleared immediately, considerable over-charging of the remainder of the cells will be necessary before the faulty cell is back to normal condition. In the case of cells with bolted connections, if the removal of the "short" in the normal way presents any difficulty, the groups may be separated and lifted out for examination and treatment.

# Buckling of Plates.

Once buckling of the plates of a cell, through any cause, has become noticeable, it increases at a very much greater rate than during the early stages. This is due to the fact that the varying separation of the plates causes considerable variation in the distribution of the charge. As a result some parts are overworked and others are underworked. This again causes unequal expansion of the plates and further buckling. It is obvious, therefore, that the most satisfactory results will be obtained from a method of treatment under which buckling is prevented.

Even if the buckling is discovered at an early stage, the only treatment then possible (straightening the plates) is far from satisfactory. Straightening merely compresses the material on one side of the plate and stretches that on the other and, in a few cycles, the plates will be found to be returning to their buckled state. After some months of service, the straightened positive plate exhibits fine cracks round the edges and would collapse if straightening were again attempted.

# Deposit.

In a properly maintained cell, the deposit accumulates at the rate of about 5/16" per annum, or, say, one inch in 3-3½ years. It varies, of course, with the number of discharges per annum and the figure given is for normal working, say, 80-120 discharges per annum. In the Department's standard cells, ample space has been allowed at the bottom of the box and, unless overcharging has been considerable, removal of the deposit should not be necessary until the positives require renewal.

# Specific Gravity fall of electrolyte.

During the life of a cell a gradual fall in gravity will be observed. This is due to a certain amount of concentrated

electrolyte which lies undisturbed at the bottom of the cell, attacking the peroxide deposit and converting it to lead sulphate. This absorbs some of the acid content and the reduction in concentration is gradually diffused throughout the electrolyte. The process is a slow one and the fall is only about 10 points in 5-6 years. The gravity may be restored by the addition of sulphuric acid after such a period. Generally this is the only circumstance necessitating the addition of acid to the electrolyte.

# Oil film.

Unless the thickness of the film is maintained, the advantages attending its use are entirely lost and its presence is then a nuisance. Normally it should be maintained at a thickness of  $\frac{1}{8}$ ", and should not require renewal more often than once in 5 years.

The foregoing cover practically all the more important of secondary cell troubles and to convey some idea of the relative monetary losses incurred by faulty treatment, the following hypothetical case has been worked out:—

It is assumed that a 40-volt, 1000 a.h. battery (2 sets) is being worked under two different conditions—"A," a satisfactory method, "B," a moderately unsatisfactory treatment. The daily exchange load is assumed to be 200 amperehours per day. The two cases are tabulated for the sake of clearness.

1)

	А.	В.
Capacity of battery dis	5 <b>-</b>	
charged	$90\% = 900 \text{ a.h.}$	60% = 600  a.h.
Daily output to exchang	ge 200 a.h.	200 a.h.
Battery discharge lasts.		з days
Discharges per annum.	40	62
Normal charge rate .	110 amp.	110 amp.
Charge	∫5 hrs. at 160 amps.	110 amps.
Charge	``   2 hrs. at 100 amps.	8 hrs. at
Total charge	1000 a.h.	88o a.h.
Overcharge	. 11%	47%
Average efficiency o	f	
charging machine	. 70%	$66\frac{2}{3}\%$
Annual power consump	)-	
tion	5400 kwh.	Sooo kwh.
Life of battery	. 20 years	7 years
Annual depreciation	. £16	£46

Combining the totals we have the following extra cost of the "B" method over the " $\Lambda$ " method:—

	£
Additional power at 2d. per unit	 22
,, distilled water at 1/- per gallon	 I
,, labour charges	 20
,, depreciation cost	 30
Less of capital (due to 300 a.h. lying idle)	 5
Total	 £78

This shows a total annual loss on operating of roughly £80 on a capital value of £320, or in other words, the value of the batteries is thrown away every four years. Any method of treatment resulting in such a loss has clearly nothing to justify its continuance and although the case selected is by no means an extreme case, the treatment outlined in the case of "B" above is not far removed from what has happened in recorded instances of battery trouble and failure.

# Life of plates.

The conditions under which batteries operate in telephone exchanges are, generally speaking, conducive to long life provided they receive proper treatment. It is misleading to compare the lives of batteries on a basis of years and the only correct comparison is on cycles of charge and discharge.

#### Pasted plates.

The life of a pasted plate varies with the thickness. A reasonable life for plates  $\frac{1}{4}$ " thick is from 600 to 800 cycles, and for plates  $\frac{1}{8}$ " thick about 150 to 200 cycles.

# Planté plates.

A good Planté positive should give not less than 1000 cycles before becoming so mechanically weak that it falls to pieces. With the larger types of plates values up to 1500 cycles should be obtainable.

# Box negatives.

These shrink in capacity during service, but should give above 2000 cycles before falling to 80% capacity.

Larger numbers of cycles may be obtained than those given above, if regular and careful attendance is given, and, if the battery is of a moderate size, the labour expended will be more than repaid by the increased life and resulting economy. On the other hand, where attendance to the batteries is made to fit in, as a sort of odd job in the routine of the exchange, the results are disappointing.

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#### APPENDIX.

Empirical Formula for Capacity of Plate (Capt. Lucas' Formula).

Capacity = 1.03 A  $\sqrt[5]{T^2}$  ampere-hours.

where

A = area of one side of plate in square inches.

T = thickness of plate in inches.

The ampere-hour value per sq. inch of surface for various thicknesses of plate is given below.

TABLE 1.

T = Thickness.	Ampere-hours per sq. in.		
0.05 in.	0.30		
0.10	0.45		
0.15	0.48		
0.20	0.54		
0.25	0.59		
0.30	0.63		
-	0.705		
•	0.772		
0.60	0.830		
0.40 0.50 0.60	0.		

TABLE II.

VARIATION OF RESISTANCE OF SULPHURIC ACID WITH CONCENTRATION. (KOLRAUSCH).

Specific Gravity.	Specific Resistance ohms cm.3		
1.100	1.90		
1.150	1.50		
1,200	1.36		
1.250	1.38		
1.300	1.46		
1.400	1.84		

TABLE III.

DENSITIES AND RELATIVE VOLUMES (LEAD = 1.00).

Material				Chemical Formula.	Density.	Relative Volume.
1 1 ( - (				Pb		7.00
Lead (not spongy)	• • •	• • •	• • •		U1.33	1.00
Litharge	•••		•••	РьО	9.3	1.21
Minium (Red Lead)				Pb <sub>3</sub> O <sub>1</sub>	8.9	1.27
Lead Peroxide				PbO <sub>2</sub>	8.4	1.35
Lead Sulphate		•••	•••	PbSO <sub>r</sub>	6.3	1.79

Note.—The amount of active material converted to lead sulphate per ampere-hour of discharge is 3.866 grams (0.135 oz.) of spongy lead on the negative plate and 4.463 grame (0.156 oz.) of lead peroxide on the positive plate, independent of the discharge rate.

The volume of electrolyte increases during charge and decreases during discharge by about 0.85 c.c. or 0.052 cu. inch per ampere-hour capacity for 1200 s.g. acid.

#### BIBLIOGRAPHY.

- "Storage Batteries." G. W. Vinal. 1st Edition, 1924.
- "The Lead Storage Battery." H. G. Brown.
- "The A.B.C. of Storage Battery Management." E. C. McKinnon.
- "Secondary Cells." R. G. De Wardt (I.P.O.E.E. Printed Paper No. 82).
- "Revue Generale de l'Electricité," Jan. 1917, and Jan., 1927. Technologic Papers No. 146 and 434. Bureau of Standards. Washington.
- "Storage Batteries in Relation to Modern Supply of Electric Lighting and Power." E. C. McKinnon, *I.E.E. Journal*, Vol. 66, May, 1928.