DRY-CHARGED LEAD-ACID BATTERIES

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The advantage of dry-charged lead acid battery over conventional types of batteries is that the battery is easily prepared for service and can be used after acid filling and without the customary first charge.

I INTRODUCTION

The term 'Dry-charged Battery' is intended to indicate that the charge is retained in the battery in dry condition. Dry charged battery is prepared by assembling formed negative plates dried under inert atmospheric conditions and dry formed positive plates made by one of the many conventional methods with dry microporous separators into dry containers, finally sealing the container and vent plugs against ingress of moisture. After filling the cells with dilute sulphuric acid the battery would have the required percentage of charge so as to crank the engine without initial charge when fitted into an automobile.

The most critical operation in the manufacture of dry charge batteries is drying the negative plates after forming. Damp spongy lead on the negative plate just after formation on exposure to open atmosphere readily oxidises. In order to retain the charge, plates must therefore be dried with minimum exposure to air. Many techniques are in vogue for conducting the drying operation on formed negative plates. In general they call for an inert atmosphere either of carbon-dioxide or nitrogen or the use of a vacuum with externally applied heat or applying superheated steam to provide the inert atmosphere and heat for drying the plates.

There is one other important technique which is fairly a recent one and employing altogether a different method for dry-charging negative plates. In this method a type of petroleum oil which is immiscible in water and has a boiling point higher than water is used as the medium for the removal of moisture from the negative plates. The coating of oil acts as an inhibitor against the oxidation of the negative active material, commonly referred to spongy lead. Batteries made out of these treated negative plates are supposed to withstand long periods of storage without loss of charge.

Some of these systems are used for drying of complete assembled groups particularly in America where most of the Battery manufacturers follow this method perhaps on certain economic considerations. But, in Europe the general practice is that the plates are formed separately in tanks and then dried as single or multiple plates. Besides, there is some potented methods that describe the inclusion of chemical additives in the oxide or wet paste. Also there is another method in which the negative plates after drying are protected from outside atmospheric oxidation with a thin film of water repellant material.

It is however essential that in order to achieve reliable long storage, without loss of charge in plates, all precautionary measures have to be taken to see that the plates are well protected from coming in contact with the outside atmosphere. This is important particularly in a place where the batteries are stored under extreme adverse weather conditions.

II BATTERY PRODUCTION

a) Preparation of Plates

Correct processing of plates is essential in that both positive and negative plates should be fully formed as the plates can only retain that charge characteristic which has been achieved by the formation process.

Positive Plates must be fully developed and free from surface bloom and must have sufficient lead peroxide content so as to match with negative plates. The plates have to be moved as fast as possible from the forming tanks where they have been covered with dilute sulphuric acid into the washing tank previously filled with water. The plates are thoroughly washed free of acid sufficiently enough until the outflowing water from the tank shows a pH

value about 4. The lead peroxide in the formed positive plates is quite stable and can therefore be dried by orthodox methods such as even drying, infra-red radiation drying etc. The only requirement of drying, is to ensure that the plates are completely dry.

Negative plates after pasting should be free from cracks, as otherwise this condition would tend to aggravate during the final drying of the formed plates and could reflect in a variable voltage performance when the battery was activated with acid. As the metallic sponge lead of the formed negative plates will rapidly oxidize if exposed to air, it is very essential to immerse the plates in water after removal from forming tanks and before transferring them to the drying process from water wash tanks. Here also the plates are washed free of acid and the pH value of outflowing water would be about 4 to 5.

A brief description of some of the important methods employed for drying negative formed plates is mentioned below :-

i) DRYING OF PLATES IN VACUUM :-

In this method of drying the plates are collected in an air tight chamber, the chamber is closed after loading plates and the air contained therein is evacuated. As soon as the pressure is reduced in the chamber, heat is transmitted through coils surrounding the walls of the chamber by radiation either by hot oil or superheated steam. The steam evolved by the evaporation of plates is sucked out by the vacuum pump and condensed in a cooling system outside the drying chamber. Drying of plates in vacuum is advantageous as it can be completed by applying relatively low temperatures which will not decompose organic expanders in the active material. Plates which have been dried in Vacuum will have more than 95% of their normal capacity if the drying process has been performed properly, and the chamber has been charged with plates in a short time.

NOTE : Drying in Vacuum can be applied for single or double plates or for complete plate groups with or without separators.

DISADVANTAGES OF THE VACUUM DRYING METHOD

The dried plates are hydrophilic in nature and therefore tend to absorb water from the surroundings. If long periods of storage are intended the plates have to be necessarily impregnated with humidity repellant substances, which of course does increase the total cost of this drying method. Another factor which is adding on to the cost of this process is that the total amount of energy needed is relatively more, as the artificial heating of objects suspended in a low pressure room needs an increased amount of heat. The motor of the Vacuum pump must be running all the time of drying.

DRYING OF PLATES IN AN ATMOSPHERE OF CO_2-gas

Principally, any inert gas atmosphere would be suitable to dry charge negative plates. Carbon-dioxide, of all gases, is advantageous because of its high density. This being heavier than air, it becomes possible to expel air out of the drying chamber by filling it with $C0_2$. In this method also a drying chamber is used in which the plates or plate groups to be dried are placed. After the chamber has been filled with plates, the chamber is closed and a stream of $C0_2$ is flown, replace most of the air. The gas inside the chamber is kept circulating by means of a cyclone which is connected with the chamber through a blow-in and take-off pipe line.

The circulating gas is heated by some suitable means at a place near the gas inlet into the drying chamber. Now the steam/$C0_2$ gaseous mixture is made to pass through a water condenser, to condense all water and the moisture free $C0_2$ gas is recirculated into the drying chamber. When there is no more of water condensation, heating is stopped and the system is allowed to cool with the gas flow still running. When an optimum safe temperature level is reached the cyclonic current of the gas is switched off, the chamber opened and plates removed.

Plates dried in $C0_2$ as above have also given a capacity more than 95% of their normal value. It is also claimed, that at the surface of the plates a very thin film of carbonate is formed which makes the plates water repellant to some extent. These plates are however required to be impregnated with hydrophobic materials if they are to be stored for a long time and in a place where heavy humid atmospheric conditions are prevailing.

III a) DRYING OF THE PLATES IN SUPERHEATED STEAM

Steam can be used as an inert atmosphere for drying formed plates. The most simple process is to place the plates inside an air tight hot chamber. By heating, steam is produced by the water content of the plates. After some time, the steam is let off, heating is stopped and at the end of drying process a stream of $C0_2$ or N_2 is passed to blow out all residual steam. When temperature of the chamber comes down to 80°C, the chamber is opened and the plates removed. Normally, maximum drying temperature is about 180°C, in this process. The maximum drying temperature depends mainly on the nature of expanders and on separators if complete groups are used for drying.

A disadvantage of this method is the relatively high end temperature which may be harmful to the plate group. There have been some attempts to overcome this advantage by a fast drying process with hot air of very high temperature. A strong breeze of hot air (approx : 240°C) is blown through a plate loaded chamber. As long as water is evaporated from the plates, the temperature of the the system remains rather low. The moment when the plates become dry the temperature inside the chamber starts shooting up and might reach a dangerous level if the hot stream of air is not switched off. The stage at which the hot air flow should be stopped is determined by measuring the temperature of blown-out gases. This drying procedure is fast (4 mts) but needs proper care and addition by the supervisory staff.

b) Another method is followed basing on the same principle of steam - drying, by a company in America, i.e Hot - Plate drying oven. About 12 plates at a time are placed on a plate holder which is put into the drying panel. The top part of the "Hot Plate" is closed and drying operation started by switching on heater. Superheated steam is evolved by the plates which dries the plates in 3 to 4 mts. When the steam evolution stops, the dry plates are removed and stacked. The heating temperature is about 180°C. Here also cut-off time must be controlled.

c) Steam drying of plates can be performed, continuously by conveying the plates through a tunnel oven in which the plates are heated by infra-red radiation. The plates are mounted on the hooks of a conveyor-chain on which they pass the length of the drying tunnel with their flat sides facing the side walls of the tunnel. The infrared heaters are mounted by these two side walls of the tunnel in such a manner that both the flat sides of the plates are exposed to the heat radiation. Fast heating of the plates should occur at the entrance part of the tunnel itself so that enough of steam is evolved to replace all air inside the chamber. The amount of heat radiating against the plates should taper down so that the other end of the tunnel is maintained at a temperature a little above the water condensation. Before passing the plates, it is the normal practice to let in steam from the external source to initiate the drying operation and to drive off air as much as possible from the tunnel.

Another system of drying with superheated steam has been employed by the Eagle-picher co-, USA the details of which are described in one of the journals "Batteries" volume 16 number 7., Page 376.

IV DRYING PLATES OR PLATE GROUPS BY IMMERSION INTO AN INERT HOT FLUID

The oil immersion method has got several advantages over other conventional types (Vacuum, steam drying etc.) of dry charging. In the first place, the negative plates, as they are heated, are protected against contact with atmospheric oxygen. The heating of the plates is uniform all over the plates area and at the same time in contact with a dry heating agent in the sense that the liquid being immiscible with respect to water does not absorb it. The plates need be heated only to temperatures at which the moisture will start vaporising. The immersion need only be adequate for the migration and forced removal of the moisture from the innermost regions of the plate outwardly into the bath from where it vaporises.

a) PERCHLORETHYLENE FLUID METHOD

Perchlorethylene is a nonflammable liquid heavier than water insoluble in water and has a boiling point of 121 C. This is used in one of the patented methods for drying-charging of formed negative plates. The treatment of negative plates before dry charging is the same throughout the entire plate processing operations upto the stage of washing them free of acid after formation.

The experimental part of this method consist of a treating tank with the liquid which is heated by a suitable device. Plates are removed at certain speed such that the plates remain immersed in a hot bath for a time interval sufficient enough to dry the plates. The dipping time depends on the temperature of the bath and the thickness of the plates. The moist vapours are passed through a series of condensers and the condensed treating liquid is pumped back into the treating zone. The plates after the removal of most of the moisture are transferred to a drying zone where the residual vapours of moisture and perchlorethylene are blown out.

Plates treated with perchlorethylene in the manner described above are moisture proof. But this method has got one disadvantage in that the treating liquid is perchlorethylene which is likely to contaminate the plates with chloride ions. The chlorine contamination of plates can be avoided if normal hydrocarbons are used in place of perchlorethylene. Described below a method using a petroleum hydrocarbon fluid whose boiling point is more than 100°C, immiscible in water and inert against plate materials.

b) In this method, the plates suspended in a rack and transferred to a pre-heated treating tank which consists of a high grade of kerosene. The temperature of the bath is maintained between 120 and 150°c.

There will be heavy gas-spray, due to volatilisation of steam. After all the moisture is expelled from the plates, the treatment liquid is pumped out and hot dry air is blown to remove all the fluid vapour from the plate surface. Certain hydrophobic materials like paraffin oil, ricinus oil, wool-fat or similar substances with a higher boiling point than water, could be added to the treating fluid, so that after the treatment, the coating of a thin film of these substances acts as an inhibitor against the oxidation of highly reactive, finely divided metallic lead.

It is claimed that the presence of such hydrophobic materials in plates upto 0.2% of the weight, of active material of the plate does not appear to have affected the quality of the plates.

c) There is one more modified process employing the same principle of oil immersion drying, patented under U. S. 3-189. 484 dated 27-7-1964 which is outlined below.

After forming and washing with water the wet negative plates are dried by immersion in a hot bath of a liquid only slightly miscible with water and which boils at a higher temperature than water. The treated plate is then suspended in a second bath containing a solution of a relatively nonvolatile material such as paraffin max, in a volatile solvent immiscible with water but miscible with the first treatment liquid. The plate after removal from the bath, is evaporated off leaving a thin protective coating of the non-volatile material on the plate.

V) Unconventional methods to produce drycharge negative plates

a) There have been attempts to add certain organic additives to the negative paste during paste mixing stage itself so that these could act as protective guard against oxidation after forming and drycharging in the usual manner.

FOR EXAMPLE :- Acrylhydroxybenzoic acid (USP. 2759036) is one such chemical which is used in the active paste itself.

b) The formed and washed plates are sprayed with a solution of natural or synthetic tannins and then dried. The solution is preferably an aqueous solution of spruce bark extract, and the anti-oxidising effect may be increased by the addition of 1-2%, 1-hydroxy -2-naphtholic acid or 2-5% Boric acid. After treatment the plates are reported to have a higher capacity, longer storage life and greater oxidation protection even in damp condition.

c) Another interesting technique is suggested by an author under his patent No.USP.2.900,431, who seems to employ a thermal reduction process of lead oxides instead of conventional electrochemical formation of spongy lead on negative plates.

The author might be having in view, to device a method to manufacture dry-charged negative plates which could eliminate the process of electroformation in acid besides to avoid the necessity of employing antioxidant agents.

In this method, the grid, which supports the active material, is made of antimonial-lead (6% Sb) and active material may be any lead compound capable of

getting reduced to metallic lead by the action of reducing gas(Ex: CO-gas) at a temperature at which the grid frame withstands (not to exceed 240°c) when antimonial lead grid is used). In order to hasten the reaction, the reduction is carried out under a moderately elevated pressure (Ex. 215 lbs per square inch).

d) Water repellant materials may be added either after drying or before or during the plate manufacture. one such method is detailed in a British Patent No. 808, 640, 1856.

While mixing of lead oxide and expanders during the preparation of active material paste, an oily substance is added in amount within the range of 0.5 to 3.0% by wt. of the dry active material. It has been found that sequence of mixing the oil with other ingredients can be interchanged depending upon one's own convenience. After curing, the plates are charged and dried following one of the conventional dry-charging process.

Negative plates prepared in accordance with this invention resist oxidation and could be used in batteries whose components are not dried well. It has been found that separators having moisture as high as 5.0 % may be used in these batteries without substantial deterioration of the charge over extended periods of storage.

Many mineral oils supplied by oil companies are used, which are identified from their Registered Trade Mark. To name some of them (1) shell Vitrea Oil No 27, (2) Esso Standard No. 40, (3) Esso 'Uniflo' (4) Esso Extra No. 1 and 3 (5) Esso Bulk Oil and Fiske (Lubriplate) Nos Etc.

The oxidation resistance of a negative plate prepared as above, increases quite rapidly within a range of 0.05 to 0.4% of oil. Afterwards, with the increase in quantity of oil the rate of resistance to oxidation is low and reaches almost the saturation point at 3-0 % of level.

It is observed that with the increase in oil content 0.75 % above the 20 Hr. capacity is decreased. But, the decrease is not much. If it is felt, that due consideration to be given to storage quality more than some nominal loss in capacity the oil may be increased above 0.75 % and upto 3.0 %. It is however understood that precautions will be taken for oils of low boiling point that the plates are not subjected to high temperatures. For higher boiling mineral oils, the usual production methods of forming the plate and the dry-charging process may be utilised.

f) Certain other fatty substances vegetables and animal organisms and containing the esters of fatty acids are also covered in the above invention to use them as Hydrophobic materials.

g) One other method is to treat the wet, formed plates with the fumes of a petroleum-oil with a boilnig point about 300°C before drying them in an inert atmosphere (Brit. Pat. 858, 325, 1959).

h) LANOLINE, is another material which is used as an addition agent in the paste and covered under British Pat. No. 863, 058, 1959.

An addition of 0.01 to 0.5 per cent of Lanoline on the basis of dryoxide, in the negative paste protects the negative plate from oxidation during drying after formation, and also greately improves resistance to oxidation during storages even under adverse conditions. The plates made out of this Lanoline are processed in the usual way and should preferably be dried in a hot vacuum oven or in an oven containing inert gas.

III OTHER GENERAL PRECUATION FOR THE MANUFACTURE OF DRY CHARGE BATTERIES

It is not enough, if the plates are prepared dry before assembling them inside a battery. Necessary care is to be taken, to see that other components like separators, containers, lids and plugs are also fully dried before the plates groups are assembled inside the batteries.

It is normal practice to seal the gas escape holes in the vent plugs to prevent ingress of moisture during transit. The plugs should be firmly screwed down preferably with rubber washers so that the sealing is made air tight.

IV TESTS

A number of tests are done both on fully assembled batteries and on negative plates. To quote some of them :

a) TESTS ON NEGATIVE PLATES :

Plates are checked for acid absorbancy by dropping acid on

to them and water repellency properties by adding water to the surface and the time noted for the liquid to penetrate into the active material. Acid absorbancy is almost instantaneous (less than 3 seconds) and water repellency well in excess of 2 hours.

b) ON BATTERIES

i) To check the proper sealing of batteries air pressure test is conducted during the normal battery assembly inspection. Each cell is checked individually by using a sensitive voltmeter of less than 1000 ohms per volt to check the dryness of the cell element.

ii) Activation Test :

After the acid is filled at room temperature the battery is left on open circuit for a period ranging from 20 mts to 1 hr to enable the plates to get soaked completely. If the battery is well dry charged the temperature rises of the electrolyte will not be more than 10°C and the gravity fall not more than 20 points.

iii) High Rate Discharge :

After 20 mts. of initial acid filling when the battery is discharged at 3 times the rated capacity. the battery should stand 3 mts. to a cut-off voltage 1 V per cell.

APPLICATIONS

i) Dry–charge batteries find useful applications in various commercial and military operations. These batteries are particularly useful in such places where even a limited facility is not readily available for charging batteries after acid filling.

ii) It is only the dry-charged batteries perferred in the export market over the conventional dry uncharged batteries.

The dry-charge battery which can be made ready for service just after acid filling is bound to attract a customer to buy this type of battery in preference to the conventional type of dry uncharged battery which has to undergo thorough time-consuming process of initial charge.