HADI-Paste-(wet) Filling-Process

Semi-automatic equipment type RPM-N5 / RPM-6

and

Fully automatic production-line type PRP-N1
Advantages of -Paste(wet)-filling

General:

This popular system is used on a worldwide basis by many of the technology leaders in the battery manufacturing industry since 1988.

High economic efficiency

Long life-cycle even under hardest operation-conditions

Reclamation rate is nearly zero

Provides both high ampere and watt-hour-efficiency

Extremely cost effective-price to performance ratio

Big battery-manufacturers have recognized upper advantages and have decided to use this proven and non-polluting system.

Environmental protection:

• Elimination of lead-dust-development resulting in no lead dust in the direct and indirect working areas.

• Provides ideal working hygiene and environmental protection.

Technical advantages:

• Process provides constant contact of the active material with the spines.
  (See following pictures)

DRY-FILLING

"HADI-PASTE-FILLING"

Bad electric contact to the centric staff from lead

After filling with paste there is very good electric contact to that centric staff from lead
Advantages of -Paste(wet)-filling

• „Spine-Growth“ is eliminated which means no deformation of the cover of the cells respectively of the electrodes and improved pole sealing.

• Can be used for high and low antimony as well calcium-alloys.

• at high-antimony alloys no contamination of negative electrodes.

• Acceptance of woven and non woven gauntlets.

• With non-woven gauntlets mud development is eliminated respectively reduced.

• At use of non-woven gauntlets possible reduction of the first charge.

• At use of non-woven gauntlets improved operation-condition of the battery reachable.

• Proven technology used on a worldwide basis with many traditional paste-recipes due to flexibility in allowing for special adjustments.

• Possible reduction of value required to hold the charged voltage resulting in reduced consumption of distilled water.

• Simple and minimum maintenance cycle up to three years.

• Substantial reduction of self-discharge - within 24 months.

• No need or requirement for artificial circulation of the electrolyte.

• The capacity of the electrodes can be fixed and or increased by simple changing of the filling-grade and special maturing process.

• Precise filling-minimum weight tolerances depending on plate-length/type (0,5% up to +-2%) of the paste-filling-weight depending on the accuracy of the paste!!

• Safe and monitored product and quality control during production. Wet fill process is very mature and produces product to the highest quality levels.

• Continuous filling of the complete plate length.

• same density of paste on the complete plate
Advantages of HADI-paste(wet)-filling

* all plate-length from 180 mm up to 630 mm can be filled automatically on the HADI-paste(wet)filling-system!

- Compatible with all types of pure and mixed lead oxides including Barton, Red Lead and Ball Mill.
Advantages of Paste(wet)-filling

Economic advantages:

• Significant cost advantages through the fully automatic-production-line from introduction of lead-bars to completion of the final positive filled plates. (fully automatic paste-filling-line PRP-N1)

• A substantial labour saving for automatic operation – requires only single operator. (fully automatic paste-filling-line PRP-N1)

References:

Country supplied units

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On the next pages we are showing a report of Mr. F.X. Mittermaier (inventor of paste-filling-system) published in Batteries International in 1996!
Advantages of Paste(wet)-filling

Battery making

It's all in the filling

The filling of positive tubular electrodes with paste offers numerous advantages to hygiene and environmental impact as well as manufacturing economics. And the utilisation of this particular process could be particularly valuable for producing the next generation of lead acid batteries for electric vehicles, claims Franz Xaver Mittermaler.

During recent years, the requirements for environmental protection have become very rigorous for the battery industry and are governed by criminal and civil legislation. Considerable efforts in the development of new technologies, and high investment are indispensable for the companies concerned, in order to allow for them to adhere to that legislation. The production areas for the manufacturing of lead accumulators, oxide production, moulding facilities, pasting, curing facilities, etc., are equipped in such a way that impacts on the environment rarely occur. The waste waters of an accumulator plant are cleaned and either returned to the rivers or maintained in a closed-loop circuit.

The only thing that was and today partially still is quite problematic is the production of positive tubular electrodes used for traction batteries and stationary accumulators. The positive active mass is contained in fabric tubes, in the centre of which a lead pencil is responsible for the supply and discharge of electrical currents.

The intermediate space is filled by means of a vibration insertion of lead oxide powder, with the air displaced through the fabric pores, subsequently drawing through the powder particles. Prevention of dust infiltration in the working environment requires considerable technical efforts.

This, however, is only partially successful, requiring the staff to wear face and respiratory masks. However, the new filling method described here allows for the utilisation of humid paste for the filling of the electrodes. Filling, closing of the plates, transportation and all other subsequent operations are carried out in an atmosphere that is totally free of dust. No manual operations are required in the fully automatic facilities currently available from HADI. The downstream processing operations on the formation installation do not cause any dust load for the environment.

For several reasons, it is quite advantageous to keep the electrodes from fully drying out. Apart from the danger of a minimum dust formation, a manufacturing disadvantage is the fact that the creation of too large cracks within the active mass may cause an interruption of the electrical contact and the active mass will not be completely formed. If required, the electrode may either be immersed in distilled water or sprayed in order to limit or prevent this effect.

Paste production

For decades, so-called pastes have been used for the filling of the grid carriers in the production of grid electrodes for lead accumulators. The pastes are produced according to very specific formulations in mixing facilities by a deliberate and controlled composition and mixing process. Over the course of time, numerous formulations have been developed in all accumulator plants. These formulations were investigated and further elaborated wherever grid electrodes were and are used, depending on the utilisation of the batteries as starter, traction or stationary batteries.

The material components are precisely defined quantities of powdery lead oxide, distilled water, sulphuric acid, and additives.

Three different versions of lead oxide powder are processed: mill dust, Barton dust and minium, all three of which are generally suitable for paste production and in particular for the tube-filling method. In order to reduce the time required for the formation and charging process, a portion of minium is added to the oxide powder. Each type of mixture on a pure minium
Advantages of 

-Paste(wet)-filling

Battery making

One of the crucial reasons for the development of the process described in this article was to allow for the utilisation of this particular technology for the production of tubular electrodes. The utilisation of the paste filling machines finally allows for the transfer of the complete know-how of the paste formulations to these types of electrodes also.

**PRECISE DEFINITION OF THE FILLING LEVEL**

The active paste is inserted into the tubes via so-called filling tubes. While the paste is pressed through the filling tubes by a paste pump, the fabric tubes are pulled away uniformly from these tubes. The lead pencils are centred inside the filling tubes and are expelled from the filling tubes at the same rate as the paste. The infinitely variable adjustment of two parameters in turn allows for a constant adjustment of the material filled in. The consistency of the paste is taken into account for the adjustment of these two parameters. The electrodes will then be filled with a weight tolerance of +/- 0.3%. This tolerance value is also ensured along the tubes as well as among the individual tubes. This means that the individual tubes as well as the electrodes in the finished cells are all subject to an equal load. Local overloading is prevented, a fact that benefits the service life of the batteries under all conditions encountered, such as charging and discharging. The fully automatic installa-

- Fig 1. Complete tubular plate line (standard)
  - feeding device
  - hydraulic duct coating machine
  - automatic grid removal
  - grid crossing and steering machine
  - tubes
  - paste filling machine
  - feed lead welding machine
  - washing device
  - weighing device
  - automatic paste pasting

- Different size electrodes
Advantages of -Paste(wet)-filling

Battery making

One of the crucial reasons to develop the process was to allow for the utilisation of this particular technology for the production of tubular electrodes.

Attempts at filling the small tubes version 1

Attempts at filling the small tubes version 2

Attempts at filling the small tubes version 3

CURING

The structure of the active mass with respect to porosity, mechanical stability and electrical properties for paste-filled electrodes is also defined by the curing process. This process is just as crucial as the formulation of the paste. Several methods and curing processes have been developed and utilised in accordance with different requirements. The curing process is a physico-chemical process inside the active mass of the electrode. Contrary to the prerequisites that are encountered during the production of starter electrodes, where the electrodes are heated until they have reached the required reaction temperature. The curing process will now continue independently. The humidity required for this purpose may either be supplied by the electrode itself or by a separate injection facility. The higher the water portion retained inside the electrode is, then the more favourably the process runs.

It is possible to partially evaluate the effect of the curing by measuring the residual portion of metallic lead in the cured electrode. The intention is, as has been mentioned before, to prevent complete drying of the active mass. A residual humidity of approximately 5% is recommended.

TUBES WITH FABRIC POUCHES

For many years, individual tubes were used for the production of tubular electrodes, then later on fabric pouches became more popular. In principle all types of tubular pouches that are currently utilised may be processed. It is even possible to use individual tubes, provided that the filling machine is converted accordingly. And no limits whatsoever exist with regard to the number of tubes, their diameter and length. In the most recent past the author's plant has started to produce positive electrodes with a tube diameter of 5 mm. The filling with paste has proved to be extremely advantageous and it has been possible to produce electrodes with a high specific capacity. High cycle stability and a long service life are further positive results. These electrodes are ideal for utilisation in batteries for electric vehicles.

Continuous development work has resulted in improvements of the fabric pouches with respect to mechanical and electrical requirements. The fabric structure has been optimised by changes of the fibre quality and weaving method. The most recently available pouches manufactured in non-woven fabric have already been filled with paste. Here the fine adjustment of the basic parameters proved to be extremely advantageous, because the material is easily deformed if subjected to a diametrical elastic load. In order to arrive at the dimensional accuracy required, it is important to adjust the paste consistency, filling pressure and filling velocity correspondingly. If fine-mesh tubular pouches or those of the aforementioned type are used, a considerable reduction of the sludge formation of active material is possible. In the case of dry filling the air present in the tubes will be displaced by the powder through the pores in the fabric so it helps if the pores are not too fine. In order not to slow down the filling process too much, finer-mesh fabric pores, however, have the advantage that the sludge formation of active mass is slowed down. If the paste filling method is used, fine-mesh tubular pouches may be utilised without any disadvantage. With the sludge formation reduced considerably with this type of electrode filling method. This is
Advantages of -Paste(wet)-filling

Battery making

expressed in the long service life of the batteries. During the paste filling, only a little water and paste are pressed through the pores of the fabric. The completely filled electrode is rinsed off in a separate washing station. The water used for rinsing is routed through a separator, where it is separated from the mass fraction, which again will be conveyed back to the filling machine. No material is lost in the process. The rinse water is in a closed circuit and requires only occasional replenishment.

EFFICIENT PRODUCTION

The paste filling process takes a relatively short time. Depending on the consistency of the paste and length of the electrodes, the filling velocity is 10 cm/sec maximum. Fully-automatic filling facilities allow for the coupling of the installation to fully automatic injection moulding machines for positive grids. The following raw materials are supplied to the installation: grid lead in the form of ingots, tubular pouches and positive active paste. The most varied alloys of grid lead may be processed. The pace of the line is determined by the moulding process. Feeding of the raw lead ingots is carried out automatically and is adapted to the requirements of the moulding process. The grid bars are automatically cut to size and sharpened in accordance with the type of electrode desired, pushed into the fabric pouch and conveyed to the filling facility. The filling operation is also fully automatic. The open ends of the filled electrodes are sealed with a plastic profile or by melting in a profile. The electrodes are rinsed in a downstream washing facility and then conveyed to the weighing station. By checking the weight it is possible to ensure tolerances of not more than +/- 0.3% maximum; larger tolerances are corrected by controlling the filling parameters. The finished electrodes are then stacked on pallets in a programmed palletising facility.

For production-related reasons, it may be required or desired to separate the two processes, i.e. grid moulding and electrode filling. And HADI manufactures filling machines which are available as individual units. The grid insertion is then the first station of the individual machine. Downstream stations handle the culling of the pencils, sharpening of the ends, cutting off of the stalks, insertion in the pouches, filling, closing, rinsing, weighing, on to palletising. This arrangement may also be desirable due to spatial or other reasons. Another version allows for the acceleration of the filling pace. The feed of the filling tubes runs parallel to the filling of the electrode. The time advantage in this case amounts to about 60% in comparison to the serial production line. The capacity is between 180 and 300 electrodes per hour. An intermediate storage of the grids on a supporting frame allows for buffering times in the combined action of the two manufacturing components and thus for a continuous production. Any malfunctions of one installation have only little effect on the performance of the other on the overall manufacturing process.

Contrary to the combined installation that operates at the pace of the moulding machine, the individual machine will make an acceleration of the pace possible that, if a rotary version is used, may be increased by 100%.

QUALITY CONSEQUENCES

Because the electrode filling level can be specified the capacity of the electrode maybe accurately determined. Despite a high energy density, an optimum porosity that allows for a quick acid balance within and outside of the electrodes is guaranteed. The desired structures, however, may only be reached by utilizing the corresponding formulations for the paste. So it is vital that the pastes are produced taking into account all hitherto available know-how. The existing knowledge derived from many years of research and trial of paste formulations should be used. Good battery manufacturers have numerous paste formulations at their disposal. The curing process after the filling is just as important. Only the proper method will give good results and it goes without saying that the existing know-how should also be made use of here. The energy densities possible give rise to optimism for the use of lead accumulators for automotive utilisation, in particular for electrically propelled automobiles.

Minor withdrawal of paste during the cut through the stitches of the web
Advantages of Paste(wet)-filling

Battery making

Bad electric contact to the centric staff from lead

The method described is ideal for the production of tubular electrodes with small tube diameters (5mm). This application allows for high energy densities of up to 45 Wh/kg. The possibility of installing several electrodes in the available cell space results in a high short-term current carrying capacity of the batteries. This is a tremendous advantage when it comes to acceleration of electrically

This is a tremendous advantage when it comes to acceleration

After filling with paste there is very good electric contact to that centric staff from lead

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