HADI-Paste-(wet) Filling-Process

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

and

Fully automatic production-line type PRP-N1

Advantages of HADI -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

Bad electric contact to the centric staff from lead

"HADI-PASTE-FILLING"

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

Advantages of HADI -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**.

100 % Red Lead with woven gauntlet

Barton with non woven gauntlet

Advantages of HADI -Paste(wet)-filling

Economic advantages:

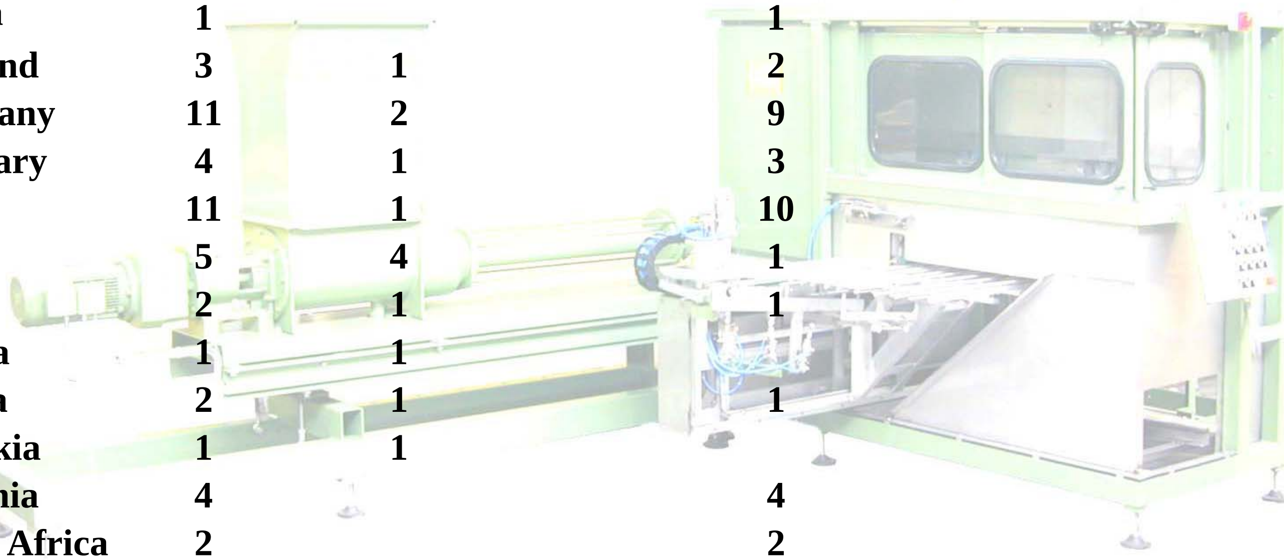
- **Significant cost advantages through the fully automatic-production-line from introduction of lead-bars to completion of the final positive filled plates. (fully automatic paste-filling-line PRP-N1)**

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

References:

Country supplied units

	Total	Semi-automatic m/c RPM	Fully automatic m/c PRP-N1
Austria	**1**	**1**	
Bulgaria	**1**	**1**	
China	**10**	**6**	**6**
Dubai	**3**		**3**
Korea	**1**		**1**
England	**3**	**1**	**2**
Germany	**11**	**2**	**9**
Hungary	**4**	**1**	**3**
Italy	**11**	**1**	**10**
India	**5**	**4**	**1**
Polen	**2**	**1**	**1**
Russia	**1**	**1**	
Serbia	**2**	**1**	**1**
Slovakia	**1**	**1**	
Slovenia	**4**		**4**
South Africa	**2**		**2**
Spain	**6**		**6**
USA	**2**		**2**



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!

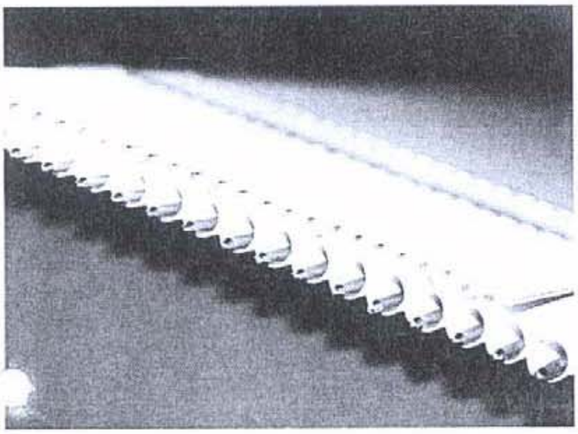
Advantages of HADI -Paste(wet)-filling

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 Mittermaier*

During recent years, the requirements for environmental protection have became 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.



Small tubes from webs of different diameters

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 to 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

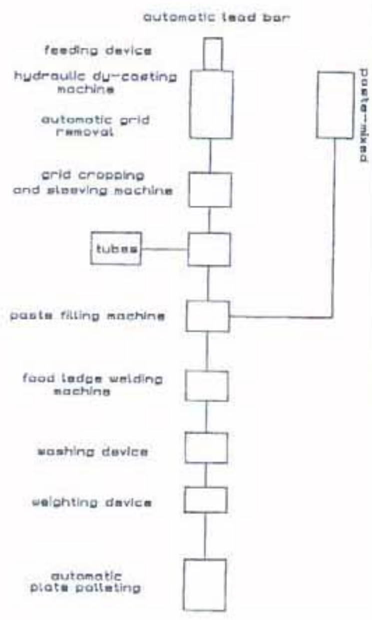
For decades, so-called pastes have been used for the filling of the grid carriers in the production of grid electrodes for lead accumulators. The pastes are produced according to very specific formulations in mixing facilities by a deliberate and controlled composition and mixing process. Over the course 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 to a pure minium paste may be processed without any problems for the tube-filling method. If pure minium is used, a single-layer formation (22 hours) is possible.

Various mixing machines are suitable for tube paste production, such as e.g. mill beaters, pan crushers or rotary mixers (that differ in the relative rotation of mixing tank and plunger as well as the horizontal or inclined position of the mixing tank). Pan crushers may only be used if the pan gears either feature a forced drive mechanism or are driven by coming into contact with the bottom of the mixer. With low-speed mixers, it is

Fig 1: Complete tubular plate line (standard)



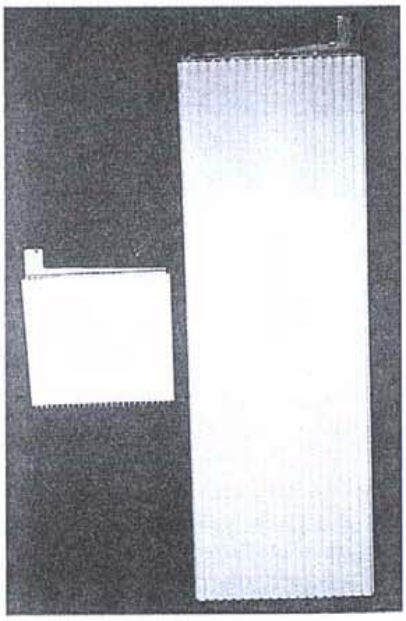
essential that attention is given to the addition of sulphuric acid. The utilisation of low-density sulphuric acid allows it to be added quickly because the reaction velocity and heating are reduced as a consequence of the higher specific portion of water caused by evaporation. The structure of the paste is critical. For low-speed mixers, coarse lead sulphate crystals are produced by a local reaction that are responsible for a sandy character of the paste. The capillary effect is thus reduced and the essential water retention capability of the paste is affected.

It is important that the pastes have a supple structure. The utilisation of proved formulations allowed for a considerable improvement of the performance and the service life of batteries. The sludge formation behaviour and thus the cycle stability have been significantly improved by the paste development for starter electrodes. The implementation of this progress to the production of tubular electrodes has had a distinct effect on their operational characteristics. 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.

> *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*

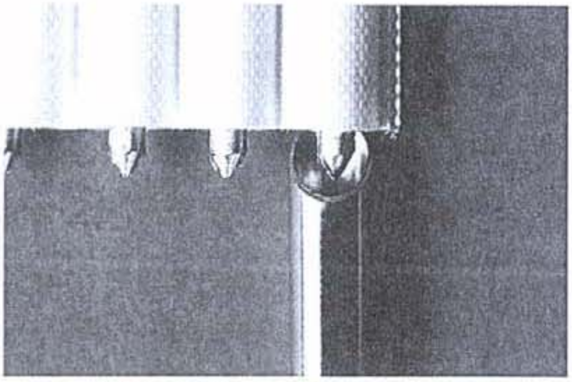
Precise definition of the filling level

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 installations manufactured by HADI ensure an automatic adjustment of the parameters, already with minimum tolerance deviations. The lead pencils are sufficiently centred by the paste. For several years, the plant operated by the author has abandoned the use of centring lugs on the lead pencils. The decision to do that proved to be advantageous for the injection moulding as well as for subsequent operations. Closure rails or melt-on rails form a leak-tight bottom closure of the tubes. Before the electrodes arrive at the curing facility, they will be stored on pallets in stacks of 30 maximum. The degree of humidity inside the electrodes is set to ensure that a subsequent separation of paste water is prevented. This will also be ensured if the electrodes are stored in a suspended manner. The stacks are covered with a blanket to ensure that the electrodes are all subject to uniform conditions and that an optimum curing process of approximately 20 hours may take place.

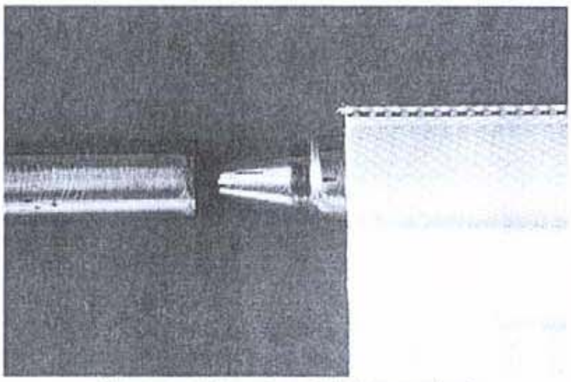


Different size electrodes

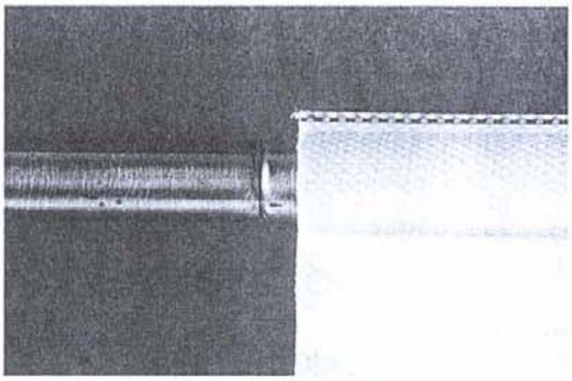
Advantages of HADI -Paste(wet)-filling



Attempts at filling the small tubes version 1



Attempts at filling the small tubes version 2



Attempts at filling the small tubes version 3

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

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 routed through a drying furnace, heated and dried at the surface after the pasting process, the paste-filled tubular electrode will leave the facility cold.

The curing process thus has to be triggered by a heating phase in a curing furnace and carried out in an environment with a controlled humidity and oxygen content, as well as a controlled temperature (based on experience). This in turn is another element that is responsible for the final quality of the performance capability and the long-term behaviour (cycle stability, sludge formation behaviour) of tubular electrodes. 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-meshed 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 HADI -Paste(wet)-filling

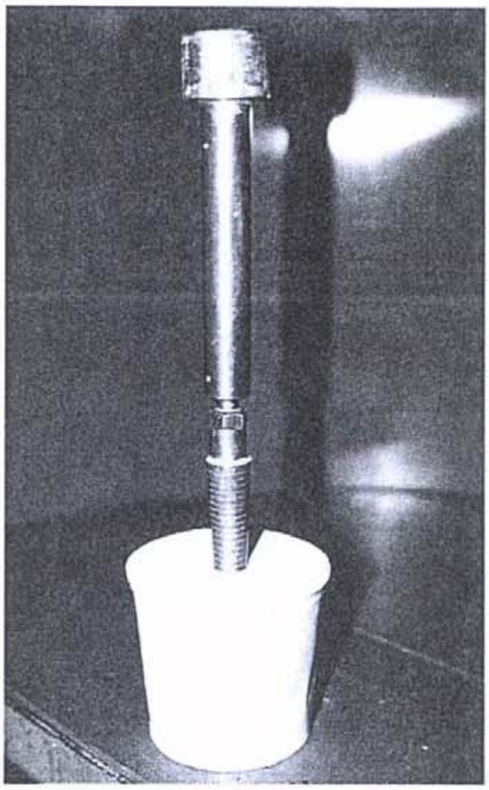
expressed in the long service life of the batteries. During the paste filling, only a little water and paste are pressed through the pores of the fabric. The completely filled electrode is rinsed off in a separate washing station. The water used for rinsing is routed through a separator, where it is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

Efficient production

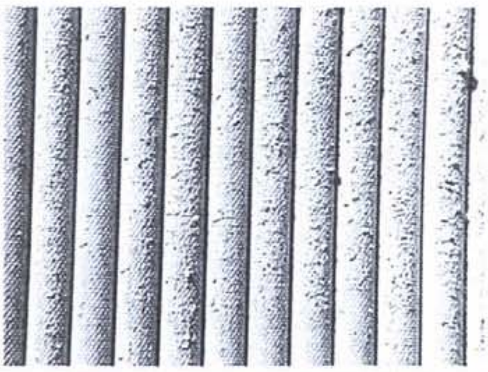
The paste filling process takes a relatively short time. Depending on the consistency of the paste and length of the electrodes, the filling velocity is 10 cm/sec. maximum. Fully-automatic filling facilities allow for the coupling of the installation to fully automatic injection moulding machines for 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 pelleting 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 cuffing of the pencils, sharpening of the ends, cutting off of the stalks, insertion in the pouches, filling, closing, rinsing, weighing, on to paletting. 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%.



Measurement of the consistency of the paste for the filling of the small tubes PEN 23-30

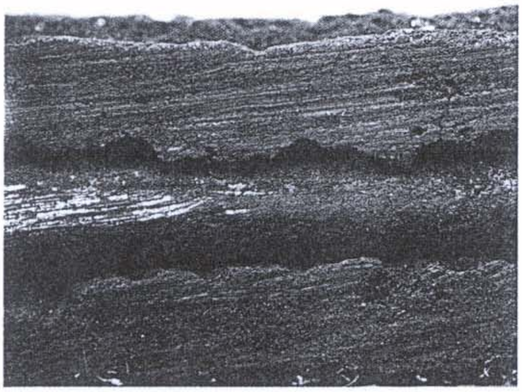


Minor withdrawal of paste during the colt through the stitches of the web

only the proper method will give good results

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 utilising 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 of lead accumulators for automotive utilisation, in particular for electrically propelled automobiles.



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 [illegible] acceleration of electrically

of the electrodes in turn ensures a quick recovery, making a large portion of the battery capacity readily available. The possibility of using tubes with a fine-mesh weaving pattern, as well as the electrodes produced in the proven curing process, provide excellent cycle stability of the electrodes. As a consequence of the paste definition, curing and forming, the active mass (lead oxide) possesses properties that are responsible for a reduction of the sludge formation tendency. If fine-mesh tubular pouches are used in addition to that, electrodes are produced that offer a high resistance to cyclic operation. This quality feature is also advantageous with respect to utilisation as a traction battery in an electrically propelled automobile.

This is a tremendous advantage when it comes to acceleration

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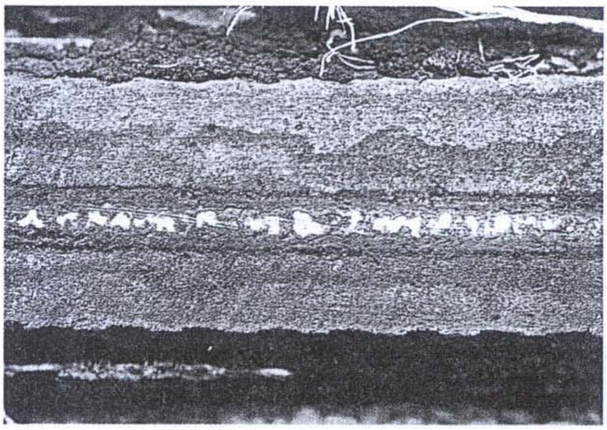

After filling with paste there is very good electric contact to that centric staff from lead